

JOURNAL OF THE CHEMICAL SOCIETY.

ABSTRACTS OF PAPERS

ON
ORGANIC, PHYSIOLOGICAL, AND
AGRICULTURAL CHEMISTRY.

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JOURNALS FROM WHICH ABSTRACTS ARE MADE.

The following is a list of Journals from which abstracts are made (directly or indirectly) by the Chemical Society and the Society of Chemical Industry. The abbreviated titles printed in italics represent Journals abstracted by the Chemical Society, those printed in roman type being abstracted by the Society of Chemical Industry. Of the former Journals those indicated by an asterisk are also abstracted by the Society of Chemical Industry.

ABBREVIATED TITLE.	JOURNAL.
<i>Abh. Böhm. Akad.</i> . . .	Abhandlungen der Böhmisches Akademie.
<i>Abh. Deut. Naturwiss. Med. Ver. Böhmen.</i>	Abhandlungen der Deutschen Naturwissenschaftlichen und Medizinischen Verein, Böhmen.
<i>Acad. Sci. Fennicae</i> . . .	Acta Societatis Scientiarum Fennicae.
<i>Agric. Bull. F. M. S.</i> . . .	Agricultural Bulletin of the Federated Malay States.
<i>Agric. Exp. Stat. Univ. Wisconsin Res. Bull.</i>	Agricultural Experimental Station, University of Wisconsin, Research Bulletin.
<i>Agric. Gaz. S. Russia</i> . . .	Agricultural Gazette of Southern Russia.
<i>Agric. J. India</i> . . .	Agricultural Journal of India.
<i>Agric. Ledger</i> . . .	Agricultural Ledger.
<i>Agric. Res. Inst., Pusa Rep. (Bull.)</i>	Agricultural Research Institute, Pusa, Report and Bulletins.
<i>Agric. and Sylvic.</i> . . .	Agriculture and Sylviculture (Petrograd).
<i>Allgem. Brau.-Hopf. Zeit.</i> . .	Allgemeine Brau- und Hopfen-Zeitung.
<i>Allgem. Gerber-Zeit.</i> . . .	Allgemeine Gerber-Zeitung.
<i>Allgem. Z. Bierbrau. u. Malzfabr.</i>	Allgemeine Zeitschrift für Bierbrauerei und Malz-fabrikation.
<i>Amat. Fotog.</i> . . .	Amator Fotografen.
<i>Amer. Brewers' J.</i> . . .	American Brewers' Journal.
<i>Amer. Brewers' Rev.</i> . . .	American Brewers' Review.
<i>Amer. J. Bot.</i> . . .	American Journal of Botany.
<i>Amer. J. Dis. Children</i> . . .	American Journal of Diseases of Children.
<i>Amer. J. Pharm.</i> . . .	American Journal of Pharmacy.
<i>Amer. J. Physiol.</i> . . .	American Journal of Physiology.
<i>Amer. J. Publ. Health</i> . . .	American Journal of Public Health.
<i>*Amer. J. Sci.</i> . . .	American Journal of Science.
<i>Amer. Mach.</i> . . .	American Machinist.
<i>Amer. Min.</i> . . .	American Mineralogist.
<i>Amer. Perf.</i> . . .	American Perfumer.
<i>Amer. Phot.</i> . . .	American Photography.
<i>Anal. Fis. Quim.</i> . . .	Anales de la Sociedad Española Física y Química.
<i>Anal. Soc. Quim. Argentina</i>	Anales de la Sociedad Química Argentina.
<i>Analyst</i> . . .	Analyst.
<i>Annalen</i> . . .	Justus Liebig's Annalen der Chemie.
<i>Ann. Bot.</i> . . .	Annals of Botany.
<i>Ann. di Bot.</i> . . .	Annali di Botanica.
<i>Ann. Chim.</i> . . .	Annales de Chimie.
<i>Ann. Chim. Analyt.</i> . . .	Annales de Chimie Analytique.
<i>Annali Chim. Appl.</i> . . .	Annali di Chimica Applicata.
<i>Ann. Ecole Agric. Montpellier.</i>	Annales de l'Ecole nationale d'Agriculture de Montpellier.
<i>Ann. Falsif.</i> . . .	Annales des Falsifications.
<i>Ann. Geol. Min. Russie</i> . . .	Annuaire de la Géologie et de la Minéralogie de Russie.
<i>Ann. hyg. pub. med. legale.</i>	Annales d'hygiène publique et de médecine légale.
<i>Ann. Inst. Mines, Petrograd</i>	Annales de l'Institut des Mines, Petrograd.
<i>Ann. Inst. Pasteur</i> . . .	Annales de l'Institut Pasteur.
<i>Ann. Inst. Polytechn., Petrograd</i>	Annales de l'Institut Polytechnique, Petrograd.
<i>Ann. Physik</i> . . .	Annalen der Physik.
<i>Ann. Physique</i> . . .	Annales de Physique.
<i>Ann. R. Staz. Chim. Agrar. Sperim.</i>	Annali della R. Stazione Chimico Agraria Sperimentale di Roma.
<i>Ann. sci. Univ. Jassy</i> . . .	Annales scientifiques de l'Université de Jassy.

ABBREVIATED TITLE.	JOURNAL.
<i>Ann. Soc. Geol. Belg. : Publ. rel. au Congo Belge</i>	Annales de la Société géologique de Belgique : Publications relatives au Congo Belge.
<i>Apoth. Zeit.</i>	Apotheker-Zeitung.
<i>App. Sci.</i>	Applied Science.
<i>Arb. Gebiet. Physik, Math. Chem.</i>	Arbeiten aus dem Gebiete der Physik, Mathematik und Chemie.
<i>Arb. Gesundh. Amt.</i>	Arbeiten aus dem Gesundheitsamte.
<i>Arch. Anat. Physiol.</i>	Archiv für Anatomie und Physiologie.
<i>Arch. Chem. Mikros.</i>	Archiv Chemie und Mikroskopie.
<i>Arch. Entw.-mech. Org.</i>	Archiv für Entwicklungsmechanik der Organismen.
<i>Arch. expt. Path. Pharm.</i>	Archiv für experimentelle Pathologie und Pharmakologie.
<i>Arch. farm. sper. sci. aff.</i>	Archivio di farmacologia sperimentale e scienze affini.
<i>Arch. Fisiol.</i>	Archivio di Fisiologia.
<i>Arch. Hyg.</i>	Archiv für Hygiene.
<i>Arch. Int. Med.</i>	The Archives of Internal Medicine.
<i>Arch. ital. Biol.</i>	Archives italiennes de Biologie.
<i>Arch. Med. Pharm. milit.</i>	Archives de Médecine et de Pharmacie militaires.
<i>Arch. Néerland.</i>	Archives Néerlandaises de sciences exactes et naturelles.
<i>Arch. Néerland. physiol.</i>	Archives Néerlandaises de physiologie de l'homme et des animaux.
<i>*Arch. Pharm.</i>	Archiv der Pharmazie.
<i>Arch. physikal. Chem. Glas. Keram.</i>	Archiv für die physikalische Chemie der Glases und der Keramischen Massen.
<i>Arch. Sci. biol. Petrograd.</i>	Archives des Sciences biologiques, Petrograd.
<i>Arch. Sci. phys. nat.</i>	Archives des Sciences physiques et naturelles.
<i>Arch. Suikerind. Ned. Indie</i>	Archief voor de Suikerindustrie in Nederlandsch-Indië.
<i>Arkiv. Kem. Min. Geol.</i>	Arkiv. för Kemi, Mineralogi och Geologi.
<i>Arm. Beton</i>	Armierter Beton.
<i>*Atti R. Accad. Lincei</i>	Atti della Reale Accademia dei Lincei.
<i>Atti R. Accad. Sci. Torino</i>	Atti della Reale Accademia delle Scienze di Torino.
<i>Atti R. Ist. Veneto Sci.</i>	Atti del Istituto Veneto di Scienze, Lettere ed Arti.
<i>Aust. Pharm. Notes</i>	Australian Pharmaceutical Notes and News.
<i>Beitr. Min. Japan</i>	Beiträge zur Mineralogie von Japan.
<i>Berg. Hüttenm. Rundsch.</i>	Berg- und Hüttenmannisches Rundschau.
<i>*Ber.</i>	Berichte der Deutschen chemischen Gesellschaft.
<i>Ber. Deut. bot. Ges.</i>	Berichte der Deutschen botanischen Gesellschaft.
<i>Ber. Deuts. pharm. Ges.</i>	Berichte der Deutschen pharmazeutischen Gesellschaft.
<i>Ber. Deut. physikal. Ges.</i>	Berichte der Deutschen physikalischen Gesellschaft.
<i>Ber. K. Sächs. Ges. Wiss.</i>	Berichte über die Verhandlungen der Königlich Sächsischen Gesellschaft der Wissenschaften.
<i>Ber. Oberhess. Ges. Natur. Heilkunde.</i>	Berichte der Oberhessischen Gesellschaft für Natur- und Heilkunde zu Giessen.
<i>Ber. Ohara Inst. landw. Forsch.</i>	Berichte des Ohara Instituts für landwirtschaftliche Forschungen.
<i>Berlin. Klin. Woch.</i>	Berliner Klinische Wochenschrift.
<i>*Bied. Zentr.</i>	Biedermann's Zentralblatt für Agrikulturchemie und rationalen Landwirtschafts-Betrieb.
<i>Biochem. Bull.</i>	Biochemical Bulletin.
<i>*Biochem. J.</i>	Biochemical Journal.
<i>*Biochem. Zeitsch.</i>	Biochemische Zeitschrift.
<i>Blätter Zucker.</i>	Blätter für Zuckerrübenbau.
<i>Bd. of Trade J.</i>	Board of Trade Journal.
<i>Bol. Acad. Nac. Ciencias, Cordoba.</i>	Boletín de la Academia Nacional des Ciencias, Cordoba.
<i>Boll. Chim. farm.</i>	Bolletino Chimico farmaceutico.
<i>Boll. Soc. Geol. Ital.</i>	Bolletino della Società Geologica Italiana.
<i>Boll. Soc. Med.-Chirurg.</i>	Bolletino della Società Medico-Chirurgica, Pavia.

ABBREVIATED TITLE.	JOURNAL.
<i>Bot. Centr.</i>	Botanisches Centralblatt.
<i>Bot. Gaz.</i>	Botanical Gazette.
<i>Brass. Malt.</i>	Brasserie et Malterie.
<i>Brau- u. Malzind.</i>	Brau- u. Malzindustrie.
<i>Braunkohle</i>	Braunkohle.
<i>Brewers' J.</i>	Brewers' Journal.
<i>Brit. and Col. Pharm.</i>	British and Colonial Pharmacist.
<i>Brit. J. Phot.</i>	British Journal of Photography.
<i>Brit. Med. J.</i>	British Medical Journal.
<i>Brit. Pat.</i>	British Patent.
<i>Buletinul Chim.</i>	Buletinul Chimie.
<i>Bul. Soc. Chim. România</i>	Buletinul Societății de Chimie din România.
<i>Bul. Soc. Romane Stiin.</i>	Buletinul Societății Romane de Stiinte.
<i>Bull. Acad. roy. Belg.</i>	Académie royale de Belgique—Bulletin de la Classe des Sciences.
<i>Bull. Acad. Sci. Cracow</i>	Bulletin international de l'Académie des Sciences de Cracovie.
<i>Bull. Acad. Sci. Petrograd.</i>	Bulletin de l'Académie Impériale des Sciences de Petrograd.
<i>Bull. Acad. Sci. Roumaine</i>	Bulletin de la Section Scientifique de l'Académie Roumaine.
<i>Bull. Agric. Intell.</i>	Bulletin of the Bureau of Agricultural Intelligence and of Plant Diseases.
<i>Bull. Assoc. Chim. Sucr.</i>	Bulletin de l'Association des Chimistes de Sucre et de Distillerie.
<i>Bull. Bureau of Standards (U.S.A.).</i>	Bulletin of the Bureau of Standards (U.S.A.).
<i>Bull. Com. Géol. Finlande.</i>	Bulletin de la Commission Géologique de Finlande.
<i>Bull. Dept. Agric. Ceylon.</i>	Bulletin of the Department of Agriculture, Ceylon.
<i>Bull. Dept. Agric. Trinidad</i>	Bulletin of the Department of Agriculture, Trinidad.
<i>Bull. Forest Exp. Stat. Meguro.</i>	Bulletin of the Forest Experiment Station, Meguro, Tokyo.
<i>Bull. gén. Thérap.</i>	Bulletin général de Thérapeutique médicale, chirurgicale, obstétricale.
<i>Bull. Geol. Inst. Univ. Upsala.</i>	Bulletin of the Geological Institution of the University of Upsala.
<i>Bull. Geol. Soc. Amer.</i>	Bulletin of the Geological Society of America.
<i>Bull. Geol. Survey, U.S.A.</i>	Bulletin of the U.S. Geological Survey.
<i>Bull. Geol. Survey, West Australia.</i>	Bulletin of the Geological Survey, West Australia.
<i>Bull. Imp. Centr. Agric. Exp. Stat. Japan.</i>	Bulletin of the Imperial Central Agricultural Experimental Station of Japan.
<i>Bull. Imp. Inst.</i>	Imperial Institute Bulletin.
<i>Bull. Johns Hopkins Hospital</i>	Bulletin of Johns Hopkins Hospital.
<i>Bull. Ranade Indus. Econ. Inst. Poona.</i>	Bulletin of the Ranade Industrial and Economic Institute, Poona.
<i>Bull. School Mines and Met., Univ. Missouri</i>	Bulletin of the School of Mines and Metallurgy, University of Missouri.
<i>Bull. Sci. Pharmacol.</i>	Bulletin des Sciences Pharmacologiques.
<i>*Bull. Soc. chim.</i>	Bulletin de la Société chimique de France.
<i>*Bull. Soc. chim. Belg.</i>	Bulletin de la Société chimique de Belgique.
<i>Bull. Soc. chim. biol.</i>	Bulletin de la Société de chimie biologique.
<i>Bull. Soc. chim. Maurice</i>	Bulletin de la Société chimique de Maurice.
<i>Bull. Soc. d'Encour.</i>	Bulletin de la Société d'Encouragement pour l'Industrie Nationale.
<i>Bull. Soc. franç. Min.</i>	Bulletin de la Société française de Minéralogie.
<i>Bull. Soc. Franç. Phot.</i>	Bulletin de la Société Française de Photographie.
<i>Bull. Soc. Ind. Mulhouse</i>	Bulletin de la Société Industrielle de Mulhouse.
<i>Bull. Soc. Ind. Nord.</i>	Bulletin de la Société Industrielle du Nord de la France.

ABBREVIATED TITLE.	JOURNAL.
Bull. Soc. Ind. Rouen . . .	Bulletin de la Société Industrielle de Rouen.
Bull. Soc. Oural. Sci. Nat. . .	Bulletin de la Société Ouralienne des Amateurs des Sciences Naturelles à Catherineberg.
Bull. Soc. Pharm. Bordeaux . .	Bulletin des Travaux de la Société de Pharmacie de Bordeaux.
Bull. Wellcome Trop. Res. Lab. .	Bulletin of the Wellcome Tropical Research Laboratory.
Cairo Sci. J.	Cairo Scientific Journal.
Canada Dept. Mines Publ. . .	Canada Department of Mines Publications.
Canadian Med. Assoc. J. . .	Canadian Medical Association Journal.
Canadian Mining J.	Canadian Mining Journal.
Caoutchouc et Gutta-Percha . .	Le Caoutchouc et le Gutta-Percha.
Cement	Cement.
*Centr. Bakt. Par.	Centralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten.
Centr. Kunstdüngerind. . . .	Centralblatt für Kunstdüngerindustrie.
Centr. Min.	Centralblatt für Mineralogie, Geologie und Palaeontologie.
Centr. Zuckerind.	Centralblatt für Zuckerindustrie.
Céramique	Céramique.
Ch. of Comm. J.	Chamber of Commerce Journal.
Chemik Polski	Chemik Polski.
Chem. App.	Chemische Apparatur.
Chem. Eng.	Chemical Engineer.
Chem. Erde	Chemie der Erde.
Chem. Ind.	Chemische Industrie.
*Chem. News	Chemical News.
Chem. Trade J.	Chemical Trade Journal.
Chem. Umschau Fett-Ind. . .	Chemische Umschau über die Fett- und Harz-Industrie.
*Chem. Weekblad	Chemisch Weekblad.
Chem.-Zeit.	Chemiker-Zeitung.
Chem. Zeitsch.	Chemische Zeitschrift.
*Chem. Zentr.	Chemisches Zentralblatt.
Chem. and Drug.	Chemist and Druggist.
*Chim. et Ind.	Chimie et Industrie.
Collegium	Collegium.
*Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Compt. rend. l'Acad. d'Agric. .	Comptes rendus des Séances de l'Académie d'Agriculture de France.
Compt. rend. Soc. Biol. . . .	Comptes rendus hebdomadaires de Séances de la Société de Biologie.
Comptes rend. Trav. Lab. Carlsberg .	Comptes rendus des Travaux de Laboratoire de Carlsberg.
D. R.-P.	Deutscher Reichs-Patent.
Dept. Chem. S. Australia, Bull. .	Department of Chemistry, South Australia, Bulletins.
Derm. Woch.	Dermatologische Wochenschrift.
Deut. Essigind.	Deutsche Essigindustrie.
Deut. Mechan. Zeit.	Deutsche Mechaniker Zeitung.
Deut. med. Woch.	Deutsche medizinische Wochenschrift.
Deut. Parfum. Zeit.	Deutsche Parfümerie Zeitung.
Deuts. Zuckerind.	Deutsche Zuckerindustrie.
Econ. Geol.	Economic Geology.
Econ. Proc. Roy. Dubl. Soc. .	Economic Proceedings of the Royal Dublin Society.
Electrician	Electrician.
Elektrochem. Zeits.	Elektrochemische Zeitschrift.
Eng. and Min. J.	Engineering and Mining Journal.
Eng. News	Engineering News.
Eng. Rec.	Engineering Record.
Engrais	L'Engrais.

ABBREVIATED TITLE.	JOURNAL.
Exper. Stat. Rec.	Experimental Station Record.
Fachl. Mitt. Öst. Tabak.	Fachliche Mitteilungen der Österreichische Tabakregie.
Farber-Zeit.	Färber-Zeitung.
Farben-Zeit.	Farben-Zeitung.
Farm	The Farm (Russia).
Fermentforsch.	Fermentforschung.
Ferrum	Ferrum.
Feuerungstechnik	Feuerungstechnik.
Flora	Flora.
Földtani Közlöny	Földtani Közlöny.
Fr. Pat.	French Patent.
Fühlings Landw. Zeit.	Fühlings Landwirtschaftliche Zeitung.
Gas	Het Gas.
Gas J.	Gas Journal.
Gas Rec.	Gas Record.
*Gazzetta	Gazzetta chimica italiana.
Geol. För. Förh.	Geologiska Föreningens i Stockholm Förhandlingar.
Geol. Mag.	Geological Magazine.
Gerber	Gerber.
Gesundheitsing.	Gesundheitsingenieur.
Gornosaw. Djelo.	Gornosawodskoje Djelo.
Gummi-Zeit.	Gummi-Zeitung.
Handl. Vijft. Nat.	Handelingen van het Vijftende Natuur.
Hawaii Agric. Exp. Stat. Bull.	Hawaii Agricultural Experiment Station Bulletins.
Heart.	Heart.
Helv. Chim. Acta	Helvetica Chimica Acta.
Hess. Landw. Zeits.	Hessische Landwirtschaftliche Zeitschrift.
Hyg. Rundsch.	Hygienische Rundschau.
Indian Forest Bull.	Indian Forest Bulletin.
Indian J. Med. Res.	Indian Journal of Medical Research.
India-rubber J.	India-rubber Journal.
Ingenieur	De Ingenieur.
Int. Mitt. Bodenk.	Internationale Mitteilungen für Bodenkunde.
Int. Sugar J.	International Sugar Journal.
Int. Z. Metallog.	Internationale Zeitschrift für Metallographie.
Int. Zeitsch. phys.-chem. Biol.	Internationale Zeitschrift für physikalisch-chemische Biologie.
Iron Steel Inst. Carnegie Schol. Mem.	Iron and Steel Institute, Carnegie Scholarship Memoirs.
Jahrb. K. K. Geol. Reichsanst.	Jahrbuch der K. K. geologischen Reichsanstalt.
Jahrb. Min.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie.
Jahrb. Min. Beil.-Bd.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie, Beilage-Band.
Jahrb. Radioaktiv. Elektr. Mik.	Jahrbuch der Radioaktivität und Elektronik.
Jahrb. wiss. Bot.	Jahrbuch für wissenschaftliche Botanik.
Jahresber. Ges. vaterl. Kultur.	Jahresbericht der schlesischen Gesellschaft für vaterländische Kultur.
Jernk. Ann.	Jernkontorets Annaler.
J. d'Agric. prat.	Journal d'Agriculture Pratique.
*J. Agric. Res.	Journal of Agricultural Research.
*J. Agric. Sci.	Journal of Agricultural Science.
J. d'Agric. Trop.	Journal d'Agriculture Tropicque.
J. Agric. Victoria	Journal of Agriculture, Victoria.
*J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Amer. Leather Chem. Assoc.	Journal of the American Leather Chemists' Association.
J. Amer. Med. Assoc.	Journal of the American Medical Association.
J. Amer. Pharm. Assoc.	Journal of the American Pharmaceutical Association.

ABBREVIATED TITLE.	JOURNAL.
J. Assoc. Off. Agric. Chem.	Journal of the Association of Official Agricultural Chemists.
*J. Biol. Chem.	Journal of Biological Chemistry, New York.
J. Board Agric.	Journal of the Board of Agriculture.
J. Canad. Min. Inst.	Journal of the Canadian Mining Institute.
J. Chem. Ind. Tokyo	See Kōgyō-Kwagaku-Zasshi.
J. Chem. Met. Soc. S. Africa	Journal of the Chemical, Metallurgical, and Mining Society of South Africa.
J. Chim. physique	Journal de Chimie physique.
J. Coll. Agric. Sapporo	Journal of the College of Agriculture, Sapporo, Japan.
J. Coll. Agric. Tohoku	Journal of the College of Agriculture, Tohoku Imperial University, Japan.
J. Coll. Agric. Tokyo	Journal of the College of Agriculture, Tokyo Imperial University, Japan.
J. Coll. Eng. Univ. Tokyo	Journal of the College of Engineering, University of Tokyo.
*J. Coll. Sci. Tokyo	Journal of the College of Science, Imperial University of Tokyo.
J. Exp. Med.	Journal of Experimental Medicine.
J. Franklin Inst.	Journal of the Franklin Institute.
J. Gasbeleucht.	Journal für Gasbeleuchtung und Wasserversorgung.
J. gen. Physiol.	Journal of general Physiology.
J. Genetics	Journal of Genetics.
J. Geol.	Journal of Geology.
J. Geol. Soc. Tokyo	Chishitsugaku Zasshi (Journal of the Geological Society of Tokyo).
J. Hygiene	Journal of Hygiene.
J. Imp. Gas Assoc. Tokyo	Journal of the Imperial Gas Association of Tokyo.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. Inst. Brewing	Journal of the Institute of Brewing.
J. Inst. Petroleum Tech.	Journal of the Institute of Petroleum Technologists.
J. Inst. Sanit. Eng.	Journal of the Institute of Sanitary Engineers.
J. Landw.	Journal für Landwirtschaft.
J. Manchester School Tech.	Journal of the Manchester School of Technology.
J. Marine Biol. Assoc. U.K.	Journal of the Marine Biological Association of the United Kingdom.
J. Med. Res.	Journal of Medical Research.
J. Path. Bact.	Journal of Pathology and Bacteriology.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Pharm. Expt. Ther.	Journal of Pharmacology and Experimental Therapeutics.
*J. Physical Chem.	Journal of Physical Chemistry.
J. Physiol.	Journal of Physiology.
J. Physiol. Path. gén.	Journal de Physiologie et de Pathologie générale.
*J. pr. Chem.	Journal für praktische Chemie.
J. Proc. Asiatic Soc. Bengal.	Journal and Proceedings of the Asiatic Society of Bengal.
J. Roy. Agric. Soc.	Journal of the Royal Agricultural Society.
J. Roy. Army Med. Corps	Journal of the Royal Army Medical Corps.
J. Roy. Hort. Soc.	Journal of the Royal Horticultural Society.
J. Roy. Soc. New South Wales.	Journal and Proceedings of the Royal Society of New South Wales.
J. Roy. Soc. West Australia	Journal of the Royal Society of West Australia.
*J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Scot. Met. Soc.	Journal of the Scottish Meteorological Society.
J. Soc. Arts	Journal of the Royal Society of Arts.
J. Soc. Dyers and Col.	Journal of the Society of Dyers and Colourists.
J. Soc. Russe Métall.	Journal de la Société Russe de Métallurgie.
J. S. African Assoc. Anal. Chem.	Journal of the South African Association of Analytical Chemists.

ABBREVIATED TITLE.	JOURNAL.
J. Textile Inst.	Journal of the Textile Institute.
J. Usines Gaz	Journal des Usines à Gaz.
J. Washington Acad. Sci. . .	Journal of the Washington Academy of Science.
J. West Scotland Iron Steel Inst.	Journal of the West of Scotland Iron and Steel Institute.
K. Svenska Vet.-Akad. Handl.	Kongliga Svenska Vetenskaps Akademiens Handlingar.
Kali	Kali.
Karbid u. Azet.	Karbid und Azetylen.
Kentucky Exp. Stat. Bull.	Kentucky Experimental Station, Bulletin.
Keram. Rundsch.	Keramisch Rundschau.
Kew Bull.	Kew Bulletin.
Kiserlet Közl.	Kiserlet Közlemények.
Klein u. Mittelbrauer	Klein und Mittelbrauer.
Kongl. Landtbr. Handl. Tidskr.	See Bull. Agric. Intell.
Kōgyō-Kwagaku-Zasshi (J. Chem. Ind. Japan).	Kōgyō-Kwagaku-Zasshi (Journal of Chemical Industry, Japan).
*Kolloid Zeitsch.	Kolloid Zeitschrift.
*Koll. Chem. Beihefte	Kolloid-chemische Beihefte.
Kosmos	Kosmos (Lemberg).
Kühn-Archiv	Kühn-Archiv.
Kunststoffe	Kunststoffe.
Lancet	The Lancet.
Landw. Jahrb.	Landwirtschaftliche Jahrbücher.
Landw. Versuchs.-Stat.	Die landwirtschaftlichen Versuchs-Stationen.
Leather Trades Rev.	Leather Trades Review.
Leather Trades Year Book . .	Leather Trades Year Book.
Leather World	Leather World.
Ledertech. Rundsch.	Ledertechnische Rundschau.
Leipzig. Monatsch. Textil-Ind.	Leipziger Monatschrift für Textil-Industrie.
Le Radium	Le Radium.
L'Ind. Chimica	L'Industria Chimica.
L'Ind. Chimique	L'Industrie Chimique.
Lilly Sci. Bull.	Lilly Scientific Bulletin.
Local Govt. Bd. Reports . . .	Local Government Board Reports.
Louisiana Bull.	Louisiana Bulletin.
Louisiana Planter	Louisiana Planter.
Lunds. Univ. Årsskr.	Lunds Universitets Års-skrift.
Math. és Termész. Ért.	Mathematikai és Természettudományi Értesítő, Budapest.
Mat. Grasses	Les Matières Grasses.
Medd. K. Vetenskapsakad. Nobel-Inst.	Meddelanden från Kongl.-Vetenskapsakademiens Nobel-Institut.
Medd. on Grönland	Meddelser on Grönland.
Med. Chron.	Medical Chronicle.
Med. Klinik	Medizinesche Klinik.
Mem. Acad. Sci. Petrograd.	Mémoires de l'Académie Impériale des Sciences de Petrograd.
Mem. Accad. Lincei	Memorie della Reale Accademia dei Lincei.
Mem. Accad. Sci. Torino . . .	Memorie della Reale Accademia delle Scienze di Torino.
Mem. Coll. Sci. Kyōtō	Memoirs of the College of Science, Kyōtō Imperial University.
Mem. Coll. Sci. and Eng. Kyōtō Imp. Univ.	Memoirs of the College of Science and Engineering, Kyōtō Imperial University.
Mem. Dept. Agric. India . . .	Memoirs of the Department of Agriculture in India.
Mem. Manchester Phil. Soc. . .	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
Mém. Poudres et Salpêtres . .	Mémoriale des Poudres et Salpêtres.

ABBREVIATED TITLE.	JOURNAL.
Mem. Soc. Ing. Civ. . . .	Mémoires de la Société des Ingénieurs Civils de France.
<i>Mem. Soc. Natur. K'iev</i> . . .	Mémoires de la Société des Naturalistes de Kiev.
<i>Mem. Soc. Toscana Sci. Nat.</i>	Memorie della Società Toscana di Scienze naturali residente in Pisa.
Metall u. Erz	Metall und Erz.
Met. and Chem. Eng. . . .	Metallurgical and Chemical Engineering.
Metallurgie	Metallurgie.
Metrop. Water Bd. Rep. . . .	Metropolitan Water Board Reports.
Milch. Zentr. . . .	Milchwirtschaftliches Zentralblatt.
<i>Min. Mag.</i>	Mineralogical Magazine and Journal of the Mineralogical Society.
Min. and Eng. Rev. . . .	Mining and Engineering Review.
Ministry of Agric. Egypt.	Ministry of Agriculture of Egypt. Technical Science
Tech. Sci. Service	Service.
Mitt. Centralst. wiss.-techn. Unters.	Mittheilungen aus der Centralstelle für wissenschaftlich-technische Untersuchungen.
Mitt. deut. Landw.-Ges. . .	Mittheilungen der deutschen Landwirtschafts-Gesellschaft.
Mitt. deut. milchwirt. Ver.	Mittheilungen des deutschen milchwirtschaftlichen Vereins.
<i>Mitt. geol. Landesanst.</i> . .	Mittheilungen der geologischen Landesanstalt von Elsass-Lothringen.
Mitt. k. Materialprüf. . . .	Mittheilungen aus dem königlichen Materialprüfungsamt zu Gross-Lichterfelde West.
Mitt. k. k. Techn. Versuchsamtes	Mittheilungen des k. k. Technischen Versuchsamtes.
<i>Mitt. med. Ges. Tokyo</i> . . .	Mittheilungen der medizinischen Gesellschaft zu Tokyo.
<i>Mitt. Naturforsch. Ges. Halle.</i>	Mittheilungen der Naturforschenden Gesellschaft zu Halle.
Molk.-Zeit. . . .	Molkerei-Zeitung.
* <i>Monatsh.</i>	Monatshefte für Chemie und verwandte Teile anderer Wissenschaften.
<i>Monatsh. Math. Physik</i> . . .	Monatshefte für Mathematik und Physik.
* <i>Mon. Sci.</i>	Moniteur Scientifique.
Montan. Rundsch. . . .	Montanische Rundschau.
<i>Month. Not. Roy. Astr. Soc.</i>	Monthly Notices of the Royal Astronomical Society, London.
<i>Münch. med. Woch.</i>	Münchener medizinische Wochenschrift.
Mycol. Zentr. . . .	Mycologisches Zentralblatt.
<i>Nachr. Ges. Wiss. Göttingen.</i>	Nachrichten von der Königlichen Gesellschaft der Wissenschaften zu Göttingen.
<i>Nature</i>	Nature.
<i>Naturwiss.</i>	Die Naturwissenschaften.
<i>Naturw. Rdsch.</i>	Naturwissenschaftliche Rundschau.
Nephthanoje Djelo	Nephthanoje Djelo.
New York Agr. Expt. Sta. Bull.	New York Agricultural Experiment Station Bulletins.
New Zealand Dominion Laby. Rept.	New Zealand Dominion Laboratory Reports.
<i>Nova Acta Soc. Sci.</i>	Nova Acta Regiae Societatis Scientiarum Upsaliensis.
<i>Nuovo Cim.</i>	Il Nuovo Cimento.
<i>Öfvers. Finska Vet.-Soc.</i> . .	Öfversigt af Finska Vetenskaps-Societetens Förhandlingar, Helsingfors.
Oelmotor	Der Oelmotor.
Oesterr. Chem.-Zeit. . . .	Oesterreichische Chemiker-Zeitung.
Oesterr. Z. Berg- u. Huttenw.	Oesterreichische Zeitschrift für Berg- und Huttenwesen.
Oil and Colour Trades J. . .	Oil and Colour Trades Journal.
Oil, Paint, and Drug Rep. .	Oil, Paint, and Drug Reporter.

ABBREVIATED TITLE.	JOURNAL.
<i>Oversigt Danske Vid. Selsk.</i>	Oversigt over det Kongelige Danske Videnskabernes Selskab Forhandlingar.
<i>P.</i>	Proceedings of the Chemical Society.
<i>Pahasapa Quart.</i>	Pahasapa Quarterly.
<i>Paper</i>	Paper.
<i>Paper Maker</i>	Paper Maker.
<i>Paper Making</i>	Paper Making.
<i>Papierfabr.</i>	Papier-Fabrikant.
<i>Papier-Zeit.</i>	Papier-Zeitung.
<i>Perf. and Essent. Oil Rec.</i>	Perfumery and Essential Oil Record.
<i>Per. spis. Sofia</i>	Periodicesko spisanie Sofia.
<i>Petroleum</i>	Petroleum.
<i>Pflüger's Archiv</i>	Archiv für die gesammte Physiologie des Menschen und der Thiere.
<i>Pharm. J.</i>	Pharmaceutical Journal.
<i>Pharm. Post.</i>	Pharmazeutische Post.
<i>Pharm. Weekblad</i>	Pharmaceutisch Weekblad.
<i>Pharm. Zeit.</i>	Pharmazeutische Zeitung.
<i>Pharm. Zentr.-h.</i>	Pharmazeutische Zentrallhalle.
<i>Pharmazevt. J.</i>	Pharmazevtizeski Journal.
<i>Phil. Mag.</i>	Philosophical Magazine (The London, Edinburgh and Dublin).
<i>Phil. Trans.</i>	Philosophical Transactions of the Royal Society of London.
<i>Philippine J. Sci.</i>	Philippine Journal of Science.
<i>Phot. Ind.</i>	Photographische Industrie.
<i>Phot. J.</i>	Photographic Journal.
<i>Phot. Korr.</i>	Photographische Korrespondenz.
<i>Phot. Rundsch.</i>	Photographische Rundschau.
<i>Physical Rev.</i>	Physical Review.
<i>Physikal. Zeitsch.</i>	Physikalische Zeitschrift.
<i>Porto Rico Exper. Stat. Bull.</i>	Porto Rico Experiment Station Bulletin.
<i>Proc. Amer. Phil. Soc.</i>	Proceedings of the American Philosophical Society.
<i>Proc. Amer. Physiol. Soc.</i>	Proceedings of the American Physiological Society.
<i>*Proc. Amer. Soc. Biol. Chem.</i>	Proceedings of the American Society of Biological Chemists.
<i>Proc. Amer. Soc. Civ. Eng.</i>	Proceedings of the American Society of Civil Engineers.
<i>Proc. Amer. Soc. Testing Materials</i>	Proceedings of American Society for Testing Materials.
<i>Proc. Amer. Wood Preservers' Assoc.</i>	Proceedings of American Wood Preservers' Association.
<i>Proc. Austral. Inst. Min. Eng.</i>	Proceedings of the Australasian Institute of Mining Engineers.
<i>Proc. Brit. Foundrymen's Assoc.</i>	Proceedings of British Foundrymen's Association.
<i>Proc. Camb. Phil. Soc.</i>	Proceedings of the Cambridge Philosophical Society.
<i>Proc. Durham Phil. Soc.</i>	Proceedings of the Durham Philosophical Society.
<i>Proc. Eng. Soc. W. Pa.</i>	Proceedings of the Engineers' Society of Western Pennsylvania.
<i>Proc. Inst. Civ. Eng.</i>	Proceedings of the Institution of Civil Engineers.
<i>Proc. Inst. Mech. Eng.</i>	Proceedings of the Institution of Mechanical Engineers.
<i>Proc. Inst. Min. and Met.</i>	Proceedings of the Institution of Mining and Metallurgy.
<i>*Proc. K. Akad. Wetensch. Amsterdam.</i>	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
<i>Proc. Nat. Acad. Sci.</i>	Proceedings of the National Academy of Sciences.
<i>Proc. Nova Scotia Inst. Sci.</i>	Proceedings of the Nova Scotia Institute of Science.
<i>Proc. Phil. Soc. Glasgow</i>	Proceedings of the Glasgow Philosophical Society.
<i>Proc. Physical Soc. London</i>	Proceedings of the Physical Society of London.

ABBREVIATED TITLE.	JOURNAL.
<i>Proc. Physiol. Soc.</i> . . .	Proceedings of the Physiological Society.
<i>Proc. Roy. Inst.</i> . . .	Proceedings of the Royal Institution of Great Britain.
<i>Proc. Roy. Irish Acad.</i> . . .	Proceedings of the Royal Irish Academy.
* <i>Proc. Roy. Soc.</i> . . .	Proceedings of the Royal Society.
<i>Proc. Roy. Soc. Edin.</i> . . .	Proceedings of the Royal Society of Edinburgh.
<i>Proc. Roy. Soc. Med.</i> . . .	Proceedings of the Royal Society of Medicine.
<i>Proc. Roy. Soc. Queensland.</i>	Proceedings of the Royal Society of Queensland.
<i>Proc. Roy. Soc. Tasmania.</i> .	Proceedings of the Royal Society of Tasmania.
<i>Proc. Soc. Chem. Ind. Victoria.</i>	Proceedings of the Society of Chemical Industry, Victoria.
<i>Proc. Soc. Exp. Biol. Med.</i> .	Proceedings of the Society for Experimental Biology and Medicine.
<i>Proc. U.S. Nat. Mus.</i> . . .	Proceedings of the United States National Museum.
<i>Proc. verb. Soc. Toscana Sci. Nat.</i>	Processi verbali Società Toscana di Scienze Naturali.
<i>Quart. J. Exp. Physiol.</i> . . .	Quarterly Journal of Experimental Physiology.
<i>Quart. J. Geol. Soc.</i> . . .	Quarterly Journal of the Geological Society.
<i>Quart. J. Med.</i> . . .	Quarterly Journal of Medicine.
<i>Queensland Agric. J.</i> . . .	Queensland Agricultural Journal.
<i>Radium in Biol. Heilkunde</i>	Radium in Biologie und Heilkunde.
<i>Rec. Australian Mus.</i> . . .	Records of the Australian Museum.
<i>Rec. trav. bot. Néerland.</i> . .	Recueil des travaux botaniques Néerlandaises.
* <i>Rec. trav. chim.</i> . . .	Recueil des travaux chimiques des Pays-Bas et de la Belgique.
<i>Rend. Accad. Sci. Fis. Mat. Napoli.</i>	Rendiconto dell' Accademia delle Scienze Fisiche e Matematiche, Napoli.
<i>Rend. Ist. Lomb. Sci. Lett.</i> .	Rendiconti dell' Istituto Lombardo di Scienze e Lettere.
<i>Rend. Soc. Chim. Ital.</i> . . .	Rendiconto della Società Chimica Italiana.
<i>Rep. Aust. Assoc. Sci.</i> . . .	Report of the Australian Association for the Advancement of Science.
<i>Rep. Brit. Assoc.</i> . . .	Report of the British Association for the Advancement of Science.
<i>Rep. Pharm.</i> . . .	Repertoire de Pharmacie.
<i>Rev. Viticult.</i> . . .	Revista Viticult.
<i>Rev. gén. Bot.</i> . . .	Revue générale de Botanique.
<i>Rev. gén. Chim. pure appl.</i>	Revue générale de Chimie pure et appliquée.
<i>Rev. Gén. Mat. Col.</i> . . .	Revue Générale des Matières Colorantes.
<i>Rev. Mét.</i> . . .	Revue de Métallurgie.
<i>Rev. Real Acad. Ciencias exact. Madrid.</i>	Revista de la Real Academia de Ciencias exactas, Fisicas y Naturales de Madrid.
<i>Riv. Min. Crist. Ital.</i> . . .	Rivista di Mineralogia e Cristallografia Italiana.
<i>Russian Mining J.</i> . . .	Russian Mining Journal.
<i>Sbornik Klubu Pri.</i> . . .	Sbornik Klubu Prirodovedeckeho (Prague).
<i>Schimmel's Rep.</i> . . .	Schimmel's Reports.
<i>Schweiz. Apoth. Zeit.</i> . . .	Schweizerische Apotheker Zeitung.
<i>Schweiz. Woch. Chem. Pharm.</i>	Schweizerische Wochenschrift für Chemie und Pharmacie.
<i>Science</i> . . .	Science.
<i>Scient. Amer.</i> . . .	Scientific American.
* <i>Sci. Ind. Rep. Roure-Bertrand Fils.</i>	Scientific and Industrial Reports of Roure-Bertrand Fils.
<i>Sci. Proc. Roy. Dubl. Soc.</i> .	Scientific Proceedings of the Royal Dublin Society.
<i>Sci. Rev. Tohoku Imp. Univ.</i>	Science Reports, Tohoku Imperial University.
<i>Sci. Trans. Roy. Dubl. Soc.</i>	Scientific Transactions of the Royal Dublin Society.
<i>Seifenfabr.</i> . . .	Der Seifenfabrikant.
<i>Seifensied. Zeit.</i> . . .	Seifensieder Zeitung.
<i>Selsk. Khoz. Les. Petrograd</i>	Selskoie Khoziaistvo i Lesovodstvo Petrograd.
<i>Shoe and Leather Rep.</i> . . .	Shoe and Leather Reporter.
<i>Silikat-Zeits.</i> . . .	Silikat-Zeitschrift.

ABBREVIATED TITLE.	JOURNAL.
<i>Sitzungsber. Ges. Naturwiss. Marburg.</i>	Sitzungsberichte der Gesellschaft zur Beförderung der gesamten Naturwissenschaften in Marburg.
<i>Sitzungsber. Heidelberger Akad. Wis.</i>	Sitzungsberichte der Heidelberger Akademie der Wissenschaften.
<i>Sitzungsber. K. Akad. Wiss. Berlin.</i>	Sitzungsberichte der Königlich Preussischen Akademie der Wissenschaften zu Berlin.
<i>Sitzungsber. K. Akad. München.</i>	Sitzungsberichte der Königlich bayerischen Akademie der Wissenschaften zu München.
<i>Sitzungsber. K. Akad. Wiss. Wien.</i>	Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften, Wien.
<i>Sitzungsber. Med. Naturwiss. Ges. Münster.</i>	Sitzungsberichte der Medizinisch-Naturwissenschaftlichen Gesellschaft zu Münster-in-Westfalens.
<i>Sitzungsber. Naturforsch. Ges. Petrograd.</i>	Sitzungsberichte der Naturforschenden Gesellschaft zu Petrograd.
<i>Sitzungsber. Naturforsch. Ges. Rostock.</i>	Sitzungsberichte der Naturforschenden Gesellschaft zu Rostock.
<i>Sitzungsber. phys. med. Ges. Erlangen.</i>	Sitzungsberichte der physikalisch-medizinischen Gesellschaft zu Erlangen.
<i>Skand. Arch. Physiol.</i>	Skandinavisches Archiv für Physiologie.
<i>Smithsonian Miscell. Coll.</i>	Smithsonian Miscellaneous Collections.
<i>Soil Sci.</i>	Soil Science.
<i>South African J. Sci.</i>	South African Journal of Science.
<i>Spezialmonats. Brau- Malz.</i>	Spezialmonatshefte für Brau- und Malzerei betriebskontrolle.
Sprechsaal.	Sprechsaal.
Stahl u. Eisen.	Stahl und Eisen.
Staz. sper. agr. ital.	Stazioni sperimentali agrarie italiane.
Strahlenther.	Strahlentherapie.
Sucr. Indig.	Sucrerie Indigène.
Süddeut. Apoth. Zeit.	Süddeutsche Apotheker Zeitung.
Suikerind.	De Suikerindustrie.
<i>Suom. Tied. Toim.</i>	Suomalaisen Tiedeakatemia Toimituskia.
<i>Svensk Kem. Tidskr.</i>	Svenska Kemisk Tidskrift.
<i>T.</i>	Transactions of the Chemical Society.
Teknikern.	Teknikern.
Tekn. Tidsk.	Teknisk Tidskrift.
Textile Col.	Textile Colourist.
Ther. Gegenw.	Die Therapie der Gegenwart.
Ther. Monatsh.	Therapeutische Monatshefte.
Tidsk. Kemi, Farm., Ter.	Tidskrift Kemi, Farm. og Terape.
Tidsk. Teknikern.	Tidskriften Teknikern.
Times Eng. Suppl.	Times Engineering Supplement.
Tonind.-Zeit.	Tonindustrie-Zeitung.
Trans. Amer. Ceram. Soc.	Transactions of the American Ceramic Society.
Trans. Amer. Electrochem. Soc.	Transactions of the American Electrochemical Society.
Trans. Amer. Foundrymen's Assoc.	Transactions of the American Foundrymen's Association.
Trans. Amer. Inst. Chem. Eng.	Transactions of the American Institute of Chemical Engineers.
Trans. Amer. Inst. Metals.	Transactions of the American Institution of Metals.
Trans. Amer. Inst. Min. Eng.	Transactions of the American Institute of Mining Engineers.
Trans. Engl. Ceram. Soc.	Transactions of the English Ceramic Society.
*Trans. Faraday Soc.	Transactions of the Faraday Society.
Trans. Inst. Metals.	Transactions of the Institute of Metals.
Trans. Iron and Steel Inst.	Transactions of the Iron and Steel Institute.
Tr. N. Eng. Inst. Min. and Met.	Transactions of the North of England Institute of Mining and Metallurgy.
Trans. New Zealand Inst.	Transactions of the New Zealand Institute.
Trans. Nova Scotia Inst. Sci.	Transactions of the Nova Scotia Institute of Science.

ABBREVIATED TITLE.	JOURNAL.
<i>Trans. Path. Soc.</i> . . .	Transactions of the Pathological Society.
<i>Trans. Roy. Irish Acad.</i> . . .	Transactions of the Royal Irish Academy.
<i>Trans. Roy. Soc. Canada</i> . . .	Transactions of the Royal Society of Canada.
<i>Trans. Roy. Soc. Edin.</i> . . .	Transactions of the Royal Society of Edinburgh.
<i>Trans. Surveyors' Inst.</i> . . .	Transactions of the Surveyors' Institute.
<i>Trav. Mus. Geol. Acad. Sci.</i> <i>Petrograd.</i>	Travaux de Musée Géologique près l'Académie Impériale des Sciences de Pétersbourg.
<i>Trav. Soc. Natur. Petrograd.</i> . . .	Travaux de la Société Impériale des Naturalistes de Pétersbourg.
<i>Tropenpflanzer</i> . . .	Tropenpflanzer.
<i>Tsch. Min. Mitt.</i> . . .	Tschermak's Mineralogische Mitteilungen.
<i>U.S. Bureau of Mines, Bull.</i> <i>and Tech. Papers.</i>	United States Bureau of Mines, Bulletins and Technical Papers.
<i>U.S. Bureau Plant Ind.</i> . . .	United States Bureau of Plant Industry.
<i>U.S. Comm. Rept.</i> . . .	United States Commerce Reports, Daily Consular and Trade Reports.
<i>U.S. Dept. Agric. Bull.</i> . . .	United States Department of Agriculture Bulletins.
<i>U.S. Hyg. Labor. Bull.</i> . . .	United States Hygienic Laboratory Bulletins.
<i>U.S. Pat.</i> . . .	United States Patent.
<i>Univ. Illinois Bull.</i> . . .	University of Illinois Bulletins.
<i>Utah Agric. Coll. Exper.</i> <i>Stat. Bull.</i>	Utah Agricultural College Experiment Station Bulletins.
<i>Ver. deut. Textilver.</i> . . .	Verein deutscher Textilveredlungsindustrie.
<i>Verh. Geol. Reichsanst.</i> <i>Wien.</i>	Verhandlungen der k. k. geologischen Reichsanstalt in Wien.
<i>Verh. Ges. deut. Naturforsch.</i> <i>Aertze.</i>	Verhandlung der Gesellschaft deutscher Naturforscher und Aerzte.
<i>Verh. Naturhist. med. Ver.</i> <i>Heidelberg.</i>	Verhandlungen des naturhistorisch-medizinischen Vereins zu Heidelberg.
<i>Verh. Naturhist. Rheinl.</i> . . .	Verhandlungen des naturhistorischen Vereins der preussischen Rheinlande und Westfalens.
<i>Verh. Physiol. Ges. Berlin</i> . . .	Verhandlungen der Physiologischen Gesellschaft zu Berlin.
<i>Verh. Schweiz. Nat. Ges.</i> . . .	Verhandlungen der Schweizerischen Naturforschenden Gesellschaft, Basel.
<i>Verslag Landb.</i> . . .	Verslag Landbouwkund Onderzoek Ryklandsbouwproefstat.
<i>Vet. Rec.</i> . . .	Veterinary Record.
<i>Vict. Mem. Mus. Geol. Surv.</i> <i>vey, Canada.</i>	Victoria Memorial Museum Geological Survey of Canada, Bulletin.
<i>Videnskab. Skrifter</i> . . .	Skrifter udgivne af Videnskabselskabet i Kristiania.
<i>Wasser u. Gas</i> . . .	Wasser und Gas.
<i>West Ind. Agric. News</i> . . .	West Indian Agricultural News.
<i>West Ind. Bull.</i> . . .	West Indian Bulletin.
<i>Westnik Sacch. Prom.</i> . . .	Westnik Saccharnoi Promyshlenosti.
<i>Wiener Klin. Woch.</i> . . .	Wiener Klinische Wochenschrift.
<i>Wiss. Abhandl. Physikal.</i> <i>Tech. Reichsanst.</i>	Wissenschaftliche Abhandlungen der Physikalisch-Technischen Reichsanstalt.
<i>Wochbl. Papierfabr.</i> . . .	Wochenblatt für Papierfabrikation.
<i>Woch. f. Brau.</i> . . .	Wochenschrift für Brauerei.
<i>Yakugakuzashi</i> . . .	Yakugakuzashi.
<i>Zeitsch. allg. Physiol.</i> . . .	Zeitschrift für allgemeine Physiologie.
<i>*Zeitsch. anal. Chem.</i> . . .	Zeitschrift für analytische Chemie.
<i>Z. angew. Chem.</i> . . .	Zeitschrift für angewandte Chemie.
<i>*Zeitsch. anorg. Chem.</i> . . .	Zeitschrift für anorganische und allgemeine Chemie.
<i>Zeitsch. Biol.</i> . . .	Zeitschrift für Biologie.
<i>Zeitsch. deut. Geol. Ges.</i> . . .	Zeitschrift der deutschen Geologischen Gesellschaft.
<i>*Zeitsch. Elektrochem.</i> . . .	Zeitschrift für Elektrochemie.
<i>Zeitsch. exp. Path. Ther.</i> . . .	Zeitschrift für experimentelle Pathologie und Therapie.
<i>Z. Farben-Ind.</i> . . .	Zeitschrift für Farben-Industrie.

ABBREVIATED TITLE.	JOURNAL.
Z. Forst- u. Jagdwesen . . .	Zeitschrift für Forst- und Jagdwesen.
Z. Gärungsphysiol. . .	Zeitschrift für Gärungsphysiologie.
Z. ges. Brauw. . .	Zeitschrift für das gesammte Brauwesen.
<i>Zeitsch. ges. exp. Med.</i> . .	Zeitschrift für die gesamte experimentelle Medizin.
Z. ges. Getreidew. . .	Zeitschrift für das gesamte Getreidewesen.
Z. ges. Schiess- u. Sprengstoffw. . .	Zeitschrift für das gesammte Schiess- und Sprengstoffwesen.
<i>Zeitsch. Hyg.</i> . .	Zeitschrift für Hygiene und Infektionskrankheiten.
<i>Zeitsch. Immunit.</i> . .	Zeitschrift für Immunitätsforschung und experimentelle Therapie.
<i>Zeitsch. Instrument.</i> . .	Zeitschrift für Instrumentenkunde.
Z. Kali . . .	Zeitschrift für Kali.
<i>Zeitsch. Kryst. Min.</i> . .	Zeitschrift für Krystallographie und Mineralogie
Z. landw. Versuchsw. Oesterr. . .	Zeitschrift für das landwirtschaftlichen Versuchswesen in Oesterreich.
Z. öffentl. Chem. . .	Zeitschrift für öffentliche Chemie.
* <i>Zeitsch. physikal. Chem.</i> . .	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
<i>Zeitsch. physikal. Chem. Unterr.</i> . .	Zeitschrift für den physikalischen und Chemischen Unterricht.
<i>Zeitsch. physiol. Chem.</i> . .	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
<i>Zeitsch. prakt. Geol.</i> . .	Zeitschrift für praktische Geologie.
Z. Spiritusind. . .	Zeitschrift für Spiritusindustrie.
Z. Unters. Nahr. Genussm. . .	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Z. Ver. deut. Zuckerind. . .	Zeitschrift des Vereins der deutschen Zucker-Industrie.
<i>Zeitsch. wiss. Mikrosk.</i> . .	Zeitschrift für wissenschaftliche Mikroskopie und mikroskopische Technik.
* <i>Zeitsch. wiss. Photochem.</i> . .	Zeitschrift für wissenschaftliche Photographie, Photo-physik und Photochemie.
Z. Zuckerind. Böhm. . .	Zeitschrift für Zuckerindustrie in Böhmen.

JOURNAL
OF
THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN
BRITISH AND FOREIGN JOURNALS.

PART I.

Organic Chemistry.

The Addition of Hydrogen Bromide to Allyl Bromide. A. F. HOLLEMAN and B. F. H. J. MATTHES (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **21**, 90—91).—In bright light, hydrogen bromide is absorbed by allyl bromide with the almost quantitative formation of trimethylene bromide, b. p. $167.1^{\circ}/760$ mm.; in the dark, on the other hand, absorption proceeds much more slowly and, whilst trimethylene bromide is the main product, considerable amounts of propylene bromide are also formed. H. W.

Monohydrochloride of Isoprene. OSSIAN ASCHAN (*Ber.*, 1918, **51**, 1303—1307).—Isoprene, which had been prepared from commercial *d*-limonene by means of the isoprene lamp and kept for four years at $4-8^{\circ}$, was fractionated and the portion, b. p. $34-35.5^{\circ}$, D_4^{20} 0.6765, was mixed with 6% of dry ether, cooled in a mixture of snow and sodium chloride, and treated with hydrogen chloride. The product, after being washed with water and dried, was fractionated. The first three fractions, b. p. $65-90^{\circ}$, were treated again in the same way. The fraction, b. p. $107-110^{\circ}$, contains *isoprene monohydrochloride*, C_5H_9Cl , b. p. 109° , D_4^{20} 0.9335, which has an odour resembling that of allyl chloride, combines with hydrogen chloride to form isoprene dihydrochloride (Bouchardat's dichloro*isopentane*), b. p. $145-146^{\circ}$, D_4^{20} 1.0654, and reacts with bromine in cold chloroform to form a yellow, viscous oil, $C_5H_9ClBr_2$, which cannot be distilled without decomposition.

The isoprene monohydrochloride, b. p. 85—91°, D 0·868, described by Boushardat in 1879, was almost certainly *tert.*-isoamyl chloride. Isoprene prepared from *d*-limonene as above contains β -methyl- Δ^{β} -butylene.
C. S.

Optically Active Propylene Glycol and Optically Active β -Hydroxybutyric Acid. EMIL ABDERHALDEN and EGON EICHWALD (*Ber.*, 1918, 51, 1312—1322).—The specific rotations of the optically active fats previously prepared (A., 1914, i, 801) are unexpectedly small, and active propylene glycol has therefore been prepared in the hope that from it will be obtained more suitable substrates for the study of ferment action.

The desired glycol cannot be isolated from the mixture obtained by the action of nitrous acid on optically active propylenediamine.

Attempts to resolve β -bromo-*n*-propylamine by tartaric, bromocamphorsulphonic, or bromosuccinic acid, formyl-leucine, or similar compounds failed, uncrystallisable syrups being obtained; the resolution of β -chloro-*n*-propylamine, however, is readily effected. A solution of allylamine hydrochloride is saturated at 0° with hydrogen chloride and heated in a sealed tube at 110—120° for five to six hours, the resulting β -chloro-*n*-propylamine is isolated and treated in ether-alcohol solution with *d*-tartaric acid (1 mol.); the precipitate, after being recrystallised ten times from hot water, yields a *d*-tartrate, m. p. 109·5°, $[\alpha]_D^{18} + 36\cdot72^\circ$ in water, from which *d*- β -chloro-*n*-propylamine hydrochloride, $C_3H_9NCl_2$, m. p. 179·5°, $[\alpha]_D^{18} + 34\cdot80^\circ$ in water, is prepared. An aqueous solution of the *d*-tartrate at about 10° is converted by sodium nitrite into *d*- β -chloro- α -propanol, b. p. 40—41°/15 mm., $[\alpha]_D^{18} + 9\cdot26^\circ$. Since the latter could not be obtained quite pure it was added to aqueous potassium hydroxide at 50—70°, and thus converted into *d*-propylene oxide, b. p. 36·5—38°, $[\alpha]_D^{18} + 12\cdot72^\circ$, which has been prepared by Le Bel in a very impure state by fermentation. *d*-Propylene oxide is extensively racemised by water, and on this account must be removed by distillation as rapidly as possible from the aqueous alkali employed in its preparation (above). When added slowly to well-cooled, anhydrous formic acid, it is converted into the formate of propylene glycol, which is readily hydrolysed by 15% hydrochloric acid, yielding *d*-propylene glycol, b. p. 95°/15 mm., $[\alpha]_D^{18} + 13\cdot71^\circ$ in water. The *d*-glycol reacts with butyryl chloride in chloroform solution to form *d*-propylene glycol dibutyrate, $C_{17}H_{20}O_4$, b. p. 95—105°/15 mm., $\alpha + 2\cdot05^\circ$ in 1-dm. tube.

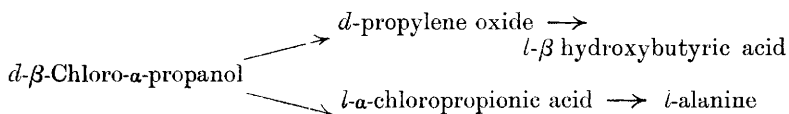
The following *l*-compounds are described: *l*- β -chloro-*n*-propylamine hydrochloride, $[\alpha]_D^{18} - 17\cdot07^\circ$ in water; *l*- β -chloro- α -propanol, $[\alpha]_D^{18} - 2\cdot92^\circ$; *l*-propylene oxide, $[\alpha]_D^{18} - 8\cdot26^\circ$; *l*-propylene glycol, $[\alpha]_D^{18} - 8\cdot97^\circ$ in water.

A synthesis of the optically active, biologically important β -hydroxybutyric acid has been effected and its configuration determined. The addition of hydrogen cyanide to *d*-propylene oxide does not lead to a satisfactory result. *d*-Propylene oxide was therefore converted by cold hydrobromic acid into *l*- β -bromoisopropyl alcohol,

$\text{OH}\cdot\text{CHMe}\cdot\text{CH}_2\text{Br}$, b. p. $45\text{--}50^\circ/15\text{ mm.}$, $\alpha - 2\cdot05^\circ$ in 1-dm. tube, which reacts readily with potassium cyanide in boiling alcohol to give *l*- β -hydroxybutyronitrile, b. p. $99\text{--}100^\circ/15\text{ mm.}$, $[\alpha]_D^{25} - 10\cdot03^\circ$ in water. The last substance is hydrolysed by hot concentrated hydrochloric acid, and yields *l*- β -hydroxybutyric acid, the sodium salt of which has $[\alpha]_D^{25} - 13\cdot28^\circ$ in water.

d- β -Chloro- α -propanol is oxidised by ammonium dichromate and dilute sulphuric acid at the ordinary temperature, and yields *l*- α -chloropropionic acid, which is converted into *l*-alanine by aqueous ammonia.

The preceding configurative relations are shown thus:

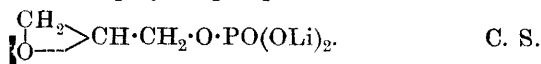


C. S.

Synthesis of Optically Active Glycerophosphoric Acid.

EMIL ABDERHALDEN and EGON EICHWALD (*Ber.*, 1918, 51 1308—1312).—Since the naturally occurring glycerophosphoric acid is optically active (Willstätter and Lüdecke, *A.*, 1904, i, 1067), one of the first steps in the synthesis of a phosphatide must be the synthesis of glycerophosphoric acid in the optically active form. The authors, employing the optically active halogenhydrins and epihydrins previously prepared by them (*A.*, 1914, i, 801), obtained unsatisfactory results when they attempted to add phosphoric acid to *l*-epihydrin alcohol, epichlorohydrin, or epibromohydrin, and unsuccessful results when they attempted to esterify monochlorohydrin or monobromohydrin with anhydrous phosphoric acid, but achieved success by using Fischer's pyridine-phosphoryl chloride method. Phosphoryl chloride is added slowly to a solution of *d*- α -bromohydrin in dry pyridine, the temperature being kept below -10° ; ice-water is added after one to two hours, the solution is shaken with sufficient silver to remove the chlorine (an excess must be avoided), filtered, treated with hydrogen sulphide, again filtered, and evaporated in a vacuum to remove the hydrogen sulphide and a portion of the pyridine. Barium hydroxide in excess is added, the mixture is diluted, and then concentrated in a vacuum to remove the remainder of the pyridine; the barium in the filtered solution is exactly precipitated with sulphuric acid, and after filtering again the filtrate is without delay treated with 10% lithium hydroxide solution, after twenty-four hours evaporated to a small volume in a vacuum, heated at 80° for one hour, cooled, neutralised with hydrobromic acid, and evaporated in a vacuum until crystals begin to appear; these are redissolved by adding a few c.c. of water, and the filtered solution is treated with alcohol. The precipitate is dissolved in water and precipitated by alcohol, and after a repetition of this treatment is free from lithium bromide. The product is

nearly pure *lithium d-glycerophosphate*, $C_6H_7O_6PLi_2$, $[\alpha]_D^{18} + 3.51^\circ$ in aqueous solution. *Lithium l-glycerophosphate* was also prepared, having $[\alpha]_D^{18} - 3.02^\circ$. By using alcoholic instead of aqueous lithium hydroxide, a glycerophosphate having $[\alpha]_D^{18} + 6.26^\circ$ was obtained, but the higher value may be due to a partial conversion of the glycerophosphate into the epihydrinphosphate,



Preparation of Ethyl Acetate from Acetaldehyde. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P., 308043; from *Chem. Zentr.*, 1918, ii, 693).—The process depends on the use of a solution of aluminium ethoxide, $\text{Al}(\text{OEt})_3$, which contains at the most only traces of halogen compounds, in an organic solvent of high boiling point, such as solvent naphtha. With such solutions, which allow the most favourable temperature to be readily maintained, the yield of practically pure ethyl acetate exceeds 85% of that theoretically possible; at the same time, the duration of the action is considerably decreased, and the consumption of aluminium ethoxide is reduced to 3–5% of the acetaldehyde. H. W.

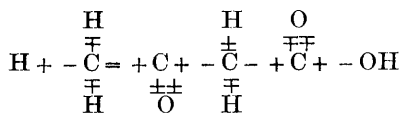
The Velocity of Hydration of the Anhydrides of some Fatty Acids. P. E. VERKADE (*Rec. trav. chim.*, 1918, **37**, 315–354).—A theoretical discussion of work already published (compare A., 1914, ii, 256; 1916, ii, 234, 607), in which the author shows that the process of hydration is much more complicated than is shown by the equation $(\text{R} \cdot \text{CO})_2\text{O} + \text{H}_2\text{O} = 2\text{R} \cdot \text{CO}_2\text{H}$. W. G.

Configuration of Organic Compounds and their Relation to Chemical and Physical Properties. II. ARTHUR MICHAEL (*J. Amer. Chem. Soc.*, 1918, **40**, 1674–1707).—A continuation of the theoretical discussion of the subject (compare A., 1918, i, 249). The relationship between the configuration of unsaturated acids and their physical properties (density, m. p., b. p., viscosity, optical activity, magnetic rotation) is examined, and the connexion between configuration and chemical properties (addition, stereomutation, catalysis, esterification) discussed. H. W.

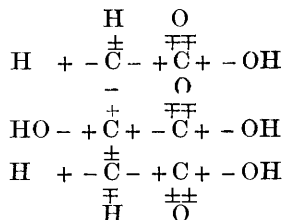
Determination of the Configuration of *cis-trans*-Isomeric Substances. J. BÖESEKEN and CHR. VAN LOON (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **21**, 80–89).—A theoretical paper, in which the methods of determining the configuration of *cis-trans* isomerides are critically discussed and their applicability to various types of compounds considered. H. W.

Electronic Constitutions of Acetoacetic and Citric Acids and some of their Derivatives. MILTON TH. HANKE and KARL K. KOESSLER (*J. Amer. Chem. Soc.*, 1918, **40**, 1726–1732).—A consideration of the formation of acetonedicarboxylic acid from citric

acid, of its relationships to acetone and acetoacetic acid, of the connexion between the latter and acetic acid, and of those between acetic acid and keten, leads the author to propose the electronic formulæ (I) and (II) for acetoacetic and citric acids respectively :



(I.)



(II.)

H. W.

Pasteur's Principle of the Relation between Molecular and Physical Asymmetry. V. Optically Active Complex Salts of Iridium-trioxalic Acid. F. M. JAEGER (*Proc. K. Akad. Wetensch Amsterdam*, 1918, **21**, 203—214).—Racemic potassium iridium oxalate, $\text{K}_3[\text{Ir}(\text{C}_2\text{O}_4)_3] \cdot 4\frac{1}{2}\text{H}_2\text{O}$ (A., 1918, i, 4), has been resolved into its optically active components by means of the strychnine salt, thus demonstrating for the first time the possibility of a partial asymmetry in the case of iridium as the central atom.

Strychnine d-iridium oxalate, $(\text{C}_{21}\text{H}_{22}\text{O}_2\text{N}_2)_3[\text{Ir}(\text{C}_2\text{O}_4)_3] \cdot 3\frac{1}{2}\text{H}_2\text{O}$, forms pale yellow, very fine needles; the corresponding *l-salt* ($+3\text{H}_2\text{O}$) crystallises in somewhat thicker needles.

d-Potassium iridium oxalate ($+ \text{H}_2\text{O}$), large orange-coloured, flattened, triangular bipyramids ($\alpha:c=1:0.9520$; $\alpha=100^\circ 20'$), has $D^{20} 2.734$; the corresponding *l-salt* is also described. As in the case of the oppositely rotating rhodium salts (A., 1918, i, 3), a non-superposable hemihedrism accompanies the contrary power of rotation.

The specific rotation of the salts in aqueous solution for differing concentrations and for light of varying wave-length has been investigated, and the results are given in a series of tables and graphs, for details of which the original communication must be consulted. In the case of the potassium salts, the slope of the graph is quite different from that found with the corresponding rhodium salt, thus showing the preponderating influence of the special nature of the central metallic atom on the specific light absorption (colour) of these salts and on the whole character of the rotation dispersion.

H. W.

Pasteur's Principle of the Relation between Molecular and Physical Asymmetry. VI. The Fission of Potassium Rhodium Malonate into its Optically Active Compounds. F. M. JAEGER and WILLIAM THOMAS (*Proc. K. Akad. Wetensch Amsterdam*, 1918, **21**, 215—224).—The resolution of *r*-potassium rhodium malonate, $[\text{Rh}(\text{C}_3\text{H}_2\text{O}_4)_3]\text{K}_3 \cdot 3\text{H}_2\text{O}$ (A., 1918, i, 4), is effected

through the cinchonine salts and subsequent decomposition of the latter by potassium iodide. *Cinchonine l-rhodium malonate* ($+ \frac{1}{2}\text{H}_2\text{O}$) is less soluble in water and less stable to heat than the corresponding *d*-salt ($+ 3\text{H}_2\text{O}$). *d*- and *l*-*Potassium rhodium malonates* form pale yellow crystals; measurements of the *l*-salt showed the crystals to belong to the monoclinic-sphenoidal class ($a:b:c=1.0637:1:1.1667$, $\beta=82^\circ 27'4''$), D_4^s 2.317.

The molecular rotation dispersion of the salts has been investigated in aqueous solution; with the potassium salts a remarkable maximum occurs at about 5800 Å.U. For wave-lengths smaller than 5800 Å.U. the rotation of the plane of polarisation increases with increasing wave-length, whilst for those greater than 5800 Å.U. it diminishes with increasing wave-lengths as in ordinary cases. In the neighbourhood of 5800 Å.U. the absorption-spectrum, however, does not manifest a single line or band. The occurrence of such anomalous rotation-dispersion seems to be theoretically explicable if the assumption may be made that at least two kinds of active ions are present.

H. W.

New Synthetic Passage from Aliphatic to Aromatic Compounds. TEL. KOMNINOS (*Compt. rend.*, 1918, 167, 781—783; *Bull. Soc. chim.*, 1918, [iv], 22, 449—455).—Malonyl chloride and acetone react together in the presence of calcium carbonate to give phloroglucinol and a compound $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}\cdot\text{COCl}$, which when boiled with water and some more calcium carbonate, in its turn is converted into phloroglucinol.

W. G.

Effect of Sodium on Mixtures of Malonic and Succinic Esters. GERALD E. K. BRANCH and H. E. HUDSON BRANCH (*J. Amer. Chem. Soc.*, 1918, 40, 1708—1713).—The investigation was undertaken in the hope of the ultimate synthesis of the compound, $\begin{array}{c} \text{CH}=\text{CH} \\ | \\ \text{CH}=\text{CH} \end{array} > \text{CH}-\text{CH} < \begin{array}{c} \text{CH}=\text{CH} \\ | \\ \text{CH}=\text{CH} \end{array}$, which might show a tendency to break down to give the cyclopentadienyl radicle. The condensation of ethyl malonate with ethyl succinate was studied as the first step in this direction. The results were not very promising, and the observations may be summarised as follows: (1) When molar mixtures of malonic and succinic esters are treated with sodium, the main product is succinylsuccinic ester. (2) When a large excess of malonic ester is used, phloroglucinoltricarboxylic ester is produced. (3) *Malonylsuccinic ester*, yellow crystals, m. p. 163°, is obtained from succinylsuccinic and malonic esters. The results are to be explained by an application of Dieckmann's theory of the reversibility of the acetoacetic ester condensation.

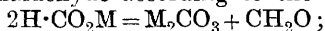
H. W.

Preparation of Derivatives of Cystine, Soluble in Water. BERNHARD STUBER (D.R.-P. 307858; from *Chem. Zentr.* 1918 ii. 574).—The sparingly soluble compounds of cystine and its derivatives with mercury, mercury chloride, or silver are dissolved in solutions of sodium chloride, sodium bromide, sodium thio-

cyanate, or lithium chloride, and the solutions are treated with an excess of acetone, methyl or ethyl alcohol, or ether; the precipitates are filtered and dried in a vacuum. Complex salts of amphoteric character are obtained which are expected to find therapeutic application. The following substances are particularly described: *cystinemercury sodium chloride*, yellow powder; *cystinemercury sodium bromide*, brown powder; *cystinemercury lithium chloride*, yellowish-white powder; *cystinemercury sodium thiocyanate*, yellowish-brown powder; *cystinesilver sodium chloride*, brown powder; *cystinemercury chloride sodium chloride*, white powder; *cystinemercury chloride sodium bromide*, brown powder. H. W.

Reducibility of Formic Acid. K. A. HOFMANN and HELGE SCHIBSTED (*Ber.*, 1918, **51**, 1389—1398).—In spite of all statements in the literature to the contrary, the authors have never obtained more than 4% of the expected yield in their attempts to reduce formic acid to formaldehyde and methyl alcohol by hydrogen under the most diverse experimental conditions. The following reducing agents were tried: (i) reduction of formic acid in aqueous solution by nascent hydrogen at ordinary pressure; the hydrogen was generated by zinc in contact with mercury, cadmium, copper, and vanadium oxide, with and without the addition of dilute sulphuric acid, by zinc and palladous chloride, by zinc dust with and without the addition of palladium, and by the platinum metals; (ii) reduction of formic acid in aqueous solution by nascent hydrogen under increased pressure; the experiments under (1) were repeated in sealed tubes at 70°, the tubes being filled with carbon dioxide before sealing; (iii) reduction with simultaneous catalytic fission of the formic acid; the experiments under (ii) were repeated in the presence of platinum metals on porous tile. C. S.

Production of Formaldehyde and Methyl Alcohol from Formates. K. A. HOFMANN and HELGE SCHIBSTED (*Ber.*, 1918, **51**, 1398—1418. Compare preceding abstract).—In the well-known decomposition of formic acid by heat and the reaction between an alkali formate and an alkali hydroxide, the principal factor controlling the course of the reactions is the striving to produce the stable hydrogen molecule. Metallic formates, however, are able, to a degree dependent on the nature of the particular metal, to yield formaldehyde according to the equation



the secondary decomposition, $\text{CH}_2\text{O} = \text{H}_2 + \text{CO}$, can be reduced to a minimum under suitable experimental conditions, and the decomposition in the presence of water, $\text{CH}_2\text{O} + \text{H}_2\text{O} = \text{CO}_2 + 2\text{H}_2$, can be prevented altogether.

The temperature at which a distinct and sustained evolution of gas begins from the formates is in general higher the more strongly basic is the metallic oxide; thus copper formate (170°) is the first and potassium formate (375°) the last member of the series of formates examined. The formaldehyde produced experiences, according to the nature of the metalliferous residue, diverse trans-

formations, of which the most important is its conversion into methyl alcohol and formic acid. In the case of the formates of strong bases, only a little formaldehyde is obtained, the main products being methyl alcohol, acetone, furfuraldehyde, empyreumatic substances, and carbon.

Zinc formate is the most suitable substance for the production of formaldehyde and methyl alcohol, and its decomposition is described in detail. Methyl formate has been detected in the products.

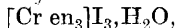
The vapour of formic acid in the presence or absence of hydrogen is converted by chemically unchangeable catalysts, such as asbestos, platinised asbestos, alumina, carbon, etc., almost exclusively into carbon monoxide and steam or carbon dioxide and hydrogen as soon as the temperature is high enough to bring the formic acid into reaction. If, however, the catalyst and the temperature of reaction are so selected that the formation of formates is rendered possible, the production of considerable quantities of formaldehyde and methyl alcohol is observed. The best catalysts for this purpose are zinc oxide and thoria. A diagram is given in which are plotted the two curves connecting the percentage of formaldehyde and the percentage of total decomposition products with the decomposition temperatures, zinc oxide being the catalyst. The two curves produced backwards meet at a point corresponding with about a 12% yield of formaldehyde and a decomposition temperature of about 245°, showing that at this temperature formaldehyde is the only primary decomposition product of formic acid. [See also *J. Soc. Chem. Ind.*, 1918, 782A.]

C. S.

The Preparation of Ethylamine and of Diethylamine.

EMIL ALPHONSE WERNER (*T.*, 1918, 113, 899—902).

Pasteur's Principle of the Relation between Molecular and Physical Asymmetry. VII. Optically Active Salts of the Triethylenediaminechromi-series. F. M. JAEGER and WILLIAM THOMAS (*Proc. K. Acad. Wetensch. Amsterdam*, 1918, 21, 225—230).—The molecular rotation dispersion of the optically active triethylenediaminechromi-iodides in aqueous solution at different concentrations has been investigated, and the results are given in a series of graphs and tables; the substances were obtained by Werner's method (*A.*, 1912, i, 417). It was not found possible to obtain measurable crystals of the active salts, partly owing to their great solubility and partly because of the readiness with which they decompose in aqueous solution, particularly under the influence of light. *r*-Triethylenediaminechromi-iodide,



forms orange to red rhombic-bipyramidal crystals ($a:b:c = 0.8632:1.0:0.8652$); the crystals are pseudo-tetragonal and per-

fectly isomorphous with the corresponding crystals of the cobalt- (A., 1915, i, 867) and of the rhodium (A., 1918, i, 7) compound.

H. W.

Biochemical Properties of Aminoglucose. A. CLEMENTI (*Arch. farm. sper. Sci. off.*, 1918, **25**, 225—230; from *Chem. Zentr.*, 1918, ii, 617).—Glucosamine hydrochloride behaves as a monobasic acid in the formol titration; Molisch's reaction is positive with the free base, but negative with the salts. Fermentation with brewer's yeast, without addition of toluene, is observed after more than seventy-two hours; obviously, foreign micro-organisms are active, possibly owing to deamination.

H. W.

Fluorides of Organo-metallic Compounds. I. Tin Trialkyl Fluorides and Tin Dialkyl Difluorides. ERICH KRAUSE (*Ber.*, 1918, **51**, 1447—1456).—The fluorides exhibit striking differences in properties from the other tin alkyl and aryl haloids. Thus the tin trialkyl fluorides are solid, crystalline, odourless substances of high m. p., which sublime before fusing, are appreciably soluble in water, giving acid solutions, and are sparingly so in indifferent organic solvents such as benzene and ether, but dissolve more readily in the alcohols and glacial acetic acid. The tin dialkyl difluorides exhibit similar properties, and, in addition, form double compounds with alkali fluorides.

The tin trialkyl fluorides are precipitated quantitatively by treating solutions of the corresponding hydroxides (Grüttner and Krause, A., 1918, i, 158) with aqueous hydrofluoric acid, but can be obtained much more conveniently by treating alcoholic solutions of the other tin trialkyl haloids with an excess of a neutral aqueous solution of potassium fluoride. The latter reaction is reversible, and a complete reconversion of the fluoride into another tin trialkyl haloid is effected by warming with the concentrated halogen acid.

Tin dialkyl difluorides are precipitated almost quantitatively by treating alcoholic solutions of the other dihaloids with the calculated quantity of potassium fluoride in neutral aqueous solution.

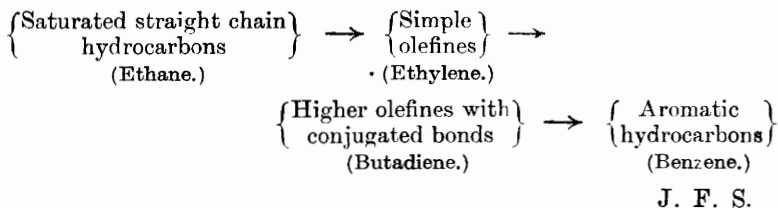
The following compounds are described. All m. p.'s were determined in closed capillary tubes. *Tin trimethyl fluoride*, SnMe_3F , colourless prisms, which begin to darken at 360° and blacken at about 375° ; *tin triethyl fluoride*, prisms, m. p. 302° (corr.); *tin tri-n-propyl fluoride*, prisms or needles, m. p. 275° (corr.); *tin triisobutyl fluoride*, prisms, m. p. 244° (corr.); *tin triisoamyl fluoride*, needles, m. p. 288° (corr.); *tin diethyl n-propyl fluoride*, long needles, m. p. 271° (corr.); *tin dimethyl difluoride*, colourless leaflets, decomp. above 360° ; *tin diethyl difluoride*, tufts of needles or rhombic plates, m. p. $287\text{--}290^\circ$ (uncorr.), sintering at about 240° (the double salt, $\text{SnEt}_2\text{F}_2 \cdot 2\text{KF}$, forms stout leaflets); *tin di-n-propyl difluoride*, leaflets, m. p. $204\text{--}205^\circ$ (uncorr.), sintering at 200° .

The tin trialkyl fluorides, which are easily obtained pure, are

available for the preparation of mixed tin tetra-alkyls, tin triethyl *n*-propyl, for example, being obtained from magnesium *n*-propyl chloride and tin triethyl fluoride in the usual way; the odour of the volatile tin trialkyl chloride is always observed, indicating that a partial exchange of the halogen atoms occurs.

Tin tetraisoamyl, prepared from tin tetrachloride and magnesium isoamyl chloride, and freed from any tin trialkyl haloid by aqueous-alcoholic potassium fluoride, has b. p. $188^{\circ}/24$ mm., D_4^{20} 1.0353, n_D 1.46946, n_D 1.47242, n_B 1.47989, n_V 1.48607 at 16.0° . C. S.

Formation of Aromatic Hydrocarbons from Natural Gas Condensates. J. G. DAVIDSON (*J. Ind. Eng. Chem.*, 1918, **10**, 901—910).—Natural gas containing chiefly ethane and propane with small quantities of butane and pentane has been subjected to the "cracking" process at various temperatures in the presence of metals. The products of the reaction are gaseous and liquid, the latter being of a tarry nature and containing aromatic hydrocarbons. Both sets of products were analysed, and the results are tabulated in the paper. The experiments show that most metals are without action on the reaction. Paraffins \rightarrow aromatic hydrocarbons. The metals nickel, iron, and cobalt are negative catalysts for the above reaction, but accelerate markedly the reaction paraffins \rightarrow carbon + hydrogen. The effect of pressure and temperature on the reaction has been studied, and it is shown that the temperature 850° is the most favourable for the production of liquid tar, and that the formation of complex aromatic substances increases with the temperature. Increase of pressure inhibits the formation of tar, whilst diminished pressure increases the yield of unsaturated substances, but also decreases the actual yield of tar. Butadiene has been isolated in fairly large amounts from the unsaturated compounds produced in the thermal decomposition of the natural gas condensate. Acetylene is without action in the formation of aromatic hydrocarbons. Tar containing aromatic substances has been produced from the "cracking" of a mixture of butadiene and ethylene. The most probable reaction for the formation of aromatic substances from natural gas condensate is:



Dinitro-derivatives of *p*-Dichlorobenzene. 1:4-Dichloro-2:5-dinitrobenzene. EDITH H. NASON (*J. Amer. Chem. Soc.*, 1918, **40**, 1602—1605).—Of the possible 1:4-dichlorodinitrobenzenes, 1:4-dichloro-2:6-dinitrobenzene, m. p. 104° , has been

previously described and fully orientated; a second isomeride, m. p. 101° , has also been obtained, but its constitution has not been elucidated. The author now shows that all three isomerides are formed when *p*-dichlorobenzene is nitrated with a mixture of concentrated sulphuric and fuming nitric acids, and that the chief product is the previously unknown 1:4-dichloro-2:5-dinitrobenzene, fine, yellow needles, m. p. 81° . The constitution of the compound is deduced from its reduction to 2:5-dichloro-*p*-phenylenediamine (compare Mohlau, A., 1886, 941), and confirmed by oxidation of the latter substance to *p*-dichlorobenzoquinone, yellow crystals, m. p. 161° .

The isomeride, m. p. 101° , must therefore be 1:4-dichloro-2:3-dinitrobenzene.

H. W.

***s*-Chlorobenzenedisulphonic Acid and some of its Derivatives.** S. C. J. OLIVIER (*Rec. trav. chim.*, 1918, **37**, 307—314).—When chlorobenzene is heated with five times its volume of fuming sulphuric acid, containing 20% of sulphur trioxide, at 300° for six hours, the product is 5-chlorobenzene-1:3-disulphonic acid, decomposing at 100° , isolated as its barium salt, $C_6H_3Cl(SO_3)_2Ba \cdot 3H_2O$. It gives a *potassium* and an *ammonium* salt, a *dichloride*, m. p. 105.5 — 106° , and a *diamide*, m. p. 223 — 224° . The dichloride, when heated in a sealed tube with phosphorus pentachloride for four hours at 200 — 210° , yields *s*-trichlorobenzene.

4-Aminobenzene-1:3-disulphonic acid, when diazotised in hydrochloric acid solution and the diazonium salt decomposed with finely divided copper, gives 4-chlorobenzene-1:3-disulphonic acid isolated as its *potassium* salt. It gives a *dichloride*, an amorphous compound, and a *diamide*, m. p. 217 — 219° .

W. G.

Studies in the Tetrahydronaphthalene Series. ARTHUR G. GREEN and FREDERICK MAURICE ROWE (T., 1918, **113**, 955—973).

Mono- and Di-chlorophenanthrenes. HÅKAN SANDQVIST and A. HAGELIN (*Ber.*, 1918, **51**, 1515—1526).—A solution of phenanthrene (containing anthracene; m. p. 97 — 102°) in carbon disulphide or carbon tetrachloride at 0° is treated slowly with an unsaturated solution of chlorine (about $1\frac{1}{2}$ mols.) in the same solvent at 0° . In addition to unchanged phenanthrene the substances obtained are (1) a compound (? trichloroanthracene), pale yellow needles, m. p. 365° (corr.), (2) 9:10-dichloroanthracene (previously described by Sandqvist in 1917 as a dichlorophenanthrene, m. p. 208 — 209°), (3) phenanthrene 9:10-dichloride, (4) 10-chlorophenanthrene, (5) pitch.

Phenanthrene 9:10-dichloride, $C_{14}H_{10}Cl_2$, decomposes appreciably into 10-chlorophenanthrene and hydrogen chloride at the ordinary temperature in the course of a few days, the decomposition being catalytically accelerated by 10-chlorophenanthrene. The m. p. is

therefore variable; a carefully purified specimen had m. p. 161° (corr.; bath at above 150° and rapidly heated), and hydrogen chloride was liberated.

Pure 10-chlorophenanthrene can be prepared from the preceding dichloride at 150 — 175° . It forms long, colourless needles, m. p. 53 — 53.5° (corr.), b. p. 370° (corr.)/737 mm., D_4^{25} 1.2310 and D_4^{25} 1.2163. It yields phenanthraquinone by oxidation, and forms a *picrate*, $C_{14}H_9Cl \cdot C_6H_2(NO_2)_3 \cdot OH$, yellow, prismatic needles, m. p. 115° (corr.).

9:10-Dichlorophenanthrene, m. p. 160 — 160.5° , which is formed by chlorinating 10-chlorophenanthrene in cold carbon disulphide or tetrachloride, yields phenanthraquinone by oxidation with boiling acetic and chromic acids.

The 3:1-dichlorophenanthrene, m. p. 124° , obtained by Sandqvist (A., 1909, i, 779) is now proved to be I-3(or 6):10-dichlorophenanthrene, m. p. 125 — 125.5° (corr.), by its formation by heating I-10-chlorophenanthrene-3(or 6)-sulphonyl chloride with phosphorus pentachloride; it yields 3-chlorophenanthraquinone, orange-yellow needles, m. p. 261° (corr.) (*monoxime*, $C_{14}H_9O_2NCl$, yellow needles, m. p. 204° [decomp.]), by oxidation with chromic and acetic acids.

An aqueous solution of potassium phenanthrene-3-sulphonate on treatment at 50° with a cold saturated aqueous solution of chlorine yields *potassium* II-10-chlorophenanthrene-3(or 6)-sulphonate, small needles, which is converted by phosphorus pentachloride into II-10-chlorophenanthrene-3(or 6)-sulphonyl chloride, grey, crystalline powder, m. p. 171° , from which II-10-chlorophenanthrene-3(or 6)-sulphonic acid, m. p. 207° , is obtained by the action of water at 140 — 150° , and II-3(or 6):10-dichlorophenanthrene, colourless needles, m. p. 113° , by the action of phosphorus pentachloride. The last-mentioned compound yields 3-chlorophenanthraquinone by oxidation. (The prefixes I and II indicate: I, that the compound contains substituents having the same orientation as those in the 10-bromophenanthrene-3(or 6)-sulphonic acid obtained by the sulphonation of 10-bromophenanthrene; II, that the orientation of the substituents in the compound is the same as in the 10-bromophenanthrene-3(or 6)-sulphonic acid obtained by the bromination of phenanthrene-3-sulphonic acid).

C. S.

Acetylation of *p*-Iodoaniline by Acetic Anhydride. P. J. MONTAGNE (*Ber.*, 1918, 51, 1489—1492).—*p*-Iodoaniline, which is very conveniently prepared by treating a solution of *p*-iodonitrobenzene in acetone with a solution of stannous chloride in hydrochloric acid (D 1.19) and basifying after the acetone has spontaneously boiled, is converted by acetic anhydride into *p*-iodoacetanilide if the mixture is gently warmed, but into *p*-iodoacetanilide and *p*-iododiacetanilide if the mixture is boiled for one-quarter to six hours; a small quantity of a *substance*, leaflets, m. p. 204.5° , is also obtained.

p-Iodoacetanilide has m. p. about 170° (rapidly heated) and 184.5° (slowly heated).

C. S.

Analgesic Substance and Process of Making. LAMBERT THORP (U.S. Pat., 1279942).—Anilides of α -bromo- α -ethylbutyric acid are prepared by treating arylamines with an acylhaloid of the acid. These anilides possess analgesic and sedative properties; they are decomposed on boiling with alkali hydroxide, the bromine being eliminated as alkali bromide. In particular, the *p*-phenetidine of α -bromo- α -ethylbutyric acid is specified; this is a colourless, crystalline compound slightly soluble in water, readily so in alcohol or ether, m. p. 54° . It has a peculiar, somewhat bitter taste. (See also *J. Soc. Chem. Ind.*, 1918.) J. F. B.

Trimorphic Change of 4-Nitroaceto-*o*-toluidide. FREDERICK DANIEL CHATTAWAY (T., 1918, 113, 897—899).

The *n*-Butylarylamines. I. The Action of *n*-Butyl Chloride on *o*- and *p*-Toluidines. JOSEPH REILLY and WILFRED JOHN HICKINBOTTOM (T., 1918, 113, 974—985).

The *n*-Butylarylamines. II. Nitration of Mono- and Di-*n*-butyl-*p*-toluidines. JOSEPH REILLY and WILFRED JOHN HICKINBOTTOM (T., 1918, 113, 985—995).

Nitro-derivatives of Diphenylamine. HUGH RYAN and THOMAS GLOVER (*Proc. Roy. Irish Acad.*, 1918, 34, [B], 97—105).—Considerable discrepancies are frequently noticed in the literature of the nitrodiphenylamines. With the object of removing these, the authors have prepared a series of substances by synthetic methods, that due to Goldberg (A., 1907, i, 1027) (in which aromatic amines are coupled with the halogen derivatives of aromatic nitro-compounds in nitrobenzene solution in the presence of potassium carbonate and cuprous iodide) being chiefly used. The following compounds are described: *p*-Nitrodiphenylamine, m. p. 133 — 134° , which, contrary to Goldberg's statement, yields a colourless solution in concentrated sulphuric acid; *m*-nitrodiphenylnitrosoamine, colourless, acicular crystals, m. p. 89 — 90° ; 2:4-dinitrodiphenylnitrosoamine, pale yellow prisms, m. p. 149 — 151° (by the action of isoamyl nitrite on a cold solution of 2:4-dinitrodiphenylamine in glacial acetic acid; at a slightly higher temperature, 2:4:2':4'-tetranitrodiphenylamine slowly separates); 3:4'-dinitrodiphenylamine, pale yellow crystals, m. p. 210 — 212° , after softening at 205° ; 2:4:6-trinitrodiphenylamine, scarlet-red prisms, m. p. 178° ; 2:4:3'-trinitrodiphenylamine, brown, platy crystals, m. p. 193 — 194° ; nitrophenyl-2:4-dinitro-*m*-tolylamine, dark yellow prisms, m. p. 199° (slight decomp.); 4-nitrophenyl-2:4-dinitro-*m*-tolylamine, straw-coloured, prismatic needles, m. p. 210° (slight decomp.); 3-nitrophenyl-2:6-dinitro-*m*-tolylamine (?), prismatic needles, m. p. 199° (decomp.); 2:4:2':4'-tetranitrodiphenylamine, brown prisms, m. p. 199 — 200° ; 2:4:6:3'-tetranitrodiphenylamine, short, yellow prisms, m. p. 210° (corr.); 2:4:6:4'-tetranitrodiphenylamine, golden-yellow prisms, m. p. 222° .

m-Nitrodiphenylnitrosoamine is converted by nitric acid in glacial acetic acid solution into trinitrodiphenylnitrosoamine, yellow, pris-

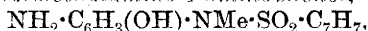
matic needles, m. p. 184—185° (decomp.), after softening at about 179°.

2:4:3'-Trinitrodiphenylamine yields *tetranitrodiphenylamine*, yellow crystals, m. p. 190°, when treated with *isoamyl* nitrite. In similar circumstances, picryl-aniline gives two compounds, one of which, m. p. 236°, is probably 2:4:6:2':4':6'-*hexanitrodiphenylamine*, whilst the other, m. p. 193—194°, appears to be 2:4:6:2':4'-*pentanitrodiphenylamine*. H. W.

The Freezing Points of Mixtures of Phenol, *o*-Cresol, *m*-Cresol, and *p*-Cresol. HARRY MEDFORTH DAWSON and CHRISTOPHER ARCHIBALD MOUNTFORD (T., 1918, **113**, 923—935).

Preparation of Hydroxy-alkyl Ethers of *p*-Acetylaminophenol or Substitution Products thereof. JOSEPH TCHERNIAC (Brit. Pat., 120081).—An alkylene or hydroxy-alkylene monohalogen-hydrin, for instance, ethylene or glycerol monochlorohydrin, is heated in water with *p*-acetylaminophenol or a substitution derivative thereof, in the presence of an equivalent quantity of alkali to combine with the halogen hydracid. For instance, 151 parts of *p*-acetylaminophenol are dissolved in an exactly equivalent quantity of 2*N*-sodium hydroxide solution, while cooling and shaking, and 81 parts of ethylene chlorohydrin are added; the mixture is heated at 60—70° for eight hours, and the β -hydroxyethyl ether separates as an oil, which crystallises on cooling. The yield is 85—90% of the theoretical, and the substance is purified by crystallising from hot water with treatment with animal charcoal. [See also *J. Soc. Chem. Ind.*, 1919, Jan.] J. F. B.

Transformation of Arylhydroxylamines into Aminophenols. F. KLAUS and O. BAUDISCH (*Ber.*, 1918, **51**, 1228—1230).—Finely powdered 3-*p*-toluenesulphonylmethylaminophenylhydroxylamine is added to a mixture of concentrated sulphuric acid and ice, water is added, and the whole is heated first on the water-bath and finally over a naked flame; the solution is filtered, neutralised with sodium carbonate, and sodium acetate is added, whereby 2-*p*-toluenesulphonylmethylamino-4-aminophenol,



m. p. 163—164°, is obtained. It develops a violet coloration with ferric chloride, reduces ammoniacal silver oxide solution, and after diazotisation couples with phenols.

In a similar manner *o*-hydroxylaminophenyl *p*-toluenesulphonate is converted into 2-amino-5-hydroxyphenyl *p*-toluenesulphonate, which is obtained in the form of the *sulphate*, colourless crystals, m. p. 162°; the *hydrochloride* forms colourless needles, m. p. 187—190°. C. S.

A Compound of Strontium Bromide and Sodium Benzoate in Galenical Pharmacy. E. CANALS and J. SERRE (*Schweiz. Apoth. Zeit.*, **56**, 318—319; from *Chem. Zentr.*, 1918, ii, 468).

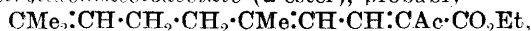
—*Strontium benzoate*, $(\text{PhCO}_2)_2\text{Sr}\cdot 3\text{H}_2\text{O}$, is obtained in small, transparent, hygroscopic needles, m. p. 410° , by mixing solutions of sodium bromide (20 grams), strontium bromide (20 grams), and sodium benzoate (12 grams), each dissolved in water (50 c.c.), diluting the mixture with an additional 150 c.c. of water, and allowing it to remain for twenty-four hours; the product is repeatedly crystallised from small quantities of hot water. At 15° , 1 part of the salt dissolves in 25.9 parts of water. H. W.

Basic Zirconyl Benzoates and Salicylates. F. P. VENABLE and F. R. BLAYLOCK (*J. Amer. Chem. Soc.*, 1918, **40**, 1746—1748).—The salts were prepared by precipitating a hot aqueous solution of zirconyl chloride with a similar solution of benzoic acid and subsequent washing with hot water. Analyses of different samples of the benzoate appear to show that under varying conditions as to concentration, etc., no single definite compound is formed. The precipitates have varying ratios between the acid radicle and the partly dehydrated zirconium hydroxide. The salicylates are notably less stable; they turn brown at 100° and become black at 160° . They appear to exhibit a tendency to form only one basic compound, in spite of varying conditions of formation, showing therein a difference from the precipitates formed with benzoic acid. H. W.

Preparation of 4-Sulphoaminobenzene-2-carboxylic [6-Amino-*m*-sulphobenzoic] Acid. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 307284, additional to D.R.-P. 296941; from *Chem. Zentr.*, 1918, ii, 574).—6-Amino-*m*-sulphobenzoic acid is conveniently prepared by the action of molecular amounts of chlorosulphonic acid and anthranilic acid dissolved in sulphuric acid monohydrate. The mixture is slowly heated to 90 — 100° , and subsequently to 130 — 140° after evolution of hydrogen chloride has ceased. Under these conditions, the monohydrate has practically no sulphonating action. H. W.

Citral Series. Condensation of Citral with Acetoacetic Ester. E. KNOEVENAGEL [with PAUL SEHLER, WILHELM STÖTZNER, RUDOLF STEINLE, GUSTAV MECHTERSHEIMER, WILHELM MAMONTOFF, and ADOLF STANG] (*J. pr. Chem.*, 1918, [ii], **97**, 288—335).—Five isomeric ethyl citrylideneacetoacetates have been obtained, the constitution of none of which has yet been definitely determined.

Ethyl citrylideneacetoacetate (α -ester), probably

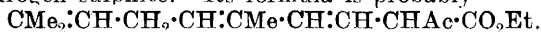


a pale yellow, faintly odorous liquid, b. p. $186^\circ/12$ mm., D_4^{20} 1.0202, n_D^{20} 1.49835, n_D^{25} 1.50645, is obtained by adding 72 drops of piperidine to a mixture of equal molecular quantities of ethyl acetoacetate and citral at about -15° , and keeping in the cold for about forty-eight hours. It changes partly to the β -ester (below) by repeated distillation or by prolonged exposure to light, dissolves easily in aqueous sodium hydrogen sulphite (therefore a double linking is

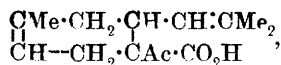
adjacent to a carbonyl group), and forms an oily *hydrobromide*, which is converted by boiling sodium carbonate solution into *ethyl α-isocitrylideneacetoacetate* (*terpinolenylacetoacetate*). This ester, which probably has the constitution $\text{CMe} \begin{smallmatrix} \text{CH}_2 \cdot \text{CHX} \\ \text{CH} \text{---} \text{CH}_2 \end{smallmatrix} \text{C}:\text{CMe}_2$

or $\text{CMe} \begin{smallmatrix} \text{CH} \cdot \text{CHX} \\ \text{CH}_2 \text{---} \text{CH}_2 \end{smallmatrix} \text{C}:\text{CMe}_2$ (where $\text{X} = \text{CHAc} \cdot \text{CO}_2\text{Et}$), forms colourless, rhombic plates, m. p. 69° , b. p. $164^\circ/12 \text{ mm.}$, $D_4^{20} 1.0056$, and is also obtained by heating the α -ester with a few c.c. of 30% sulphuric acid on the water-bath. By the addition of hydrogen bromide to the α -isoester and its removal again by sodium carbonate, the α -isoester is regenerated. The α -isoester is difficultly hydrolysed, but is converted into α -isocitrylideneacetoacetic (*terpinolenylacetoacetic*) acid, crystals, m. p. 175° (with evolution of carbon dioxide), by alcoholic potassium hydroxide at 150° , or by very concentrated, boiling aqueous potassium hydroxide. The acid, the silver salt of which reacts with ethyl iodide to form the α -isoester, is converted by heating at 180° into α -isoionone (*terpinolenylacetone*), $\text{C}_{13}\text{H}_{20}\text{O}$, a faintly yellow oil, b. p. $122^\circ/23 \text{ mm.}$, $D_4^{20} 0.9500$, $n_D^{20} 1.5021$ (*semicarbazone*, colourless crystals, m. p. 205° [decomp.]), and is converted by 10% potassium permanganate and a slight excess of sodium carbonate below 3° into a saturated acid, $\text{C}_{14}\text{H}_{24}\text{O}_5$, crystals, m. p. 192° , but yields, when a little more permanganate is used, an acid, $\text{C}_{12}\text{H}_{22}\text{O}_4$, needles, m. p. 183.5° . The latter acid is converted by boiling water into a substance, $\text{C}_{12}\text{H}_{20}\text{O}_3$, m. p. 111° (*p-bromophenylhydrazone*, m. p. 174°), and by heating in a vacuum into an isomeric substance, m. p. 94° , b. p. $180^\circ/23 \text{ mm.}$, which changes into the substance, m. p. 111° , by keeping. The oxidation of the α -isoester by chromic and acetic acids below 3° yields a substance, $\text{C}_{13}\text{H}_{18}\text{O}_4$, m. p. 42° , which forms a *semicarbazone*, yellowish-white needles, m. p. 193° . α -isoionone is oxidised by the preceding reagent to a substance, $\text{C}_{12}\text{H}_{18}\text{O}_3$, b. p. $168\text{---}171^\circ/22.5 \text{ mm.}$, m. p. 58° .

Ethyl citrylideneacetoacetate (β -ester), obtained by the repeated distillation of the α -ester in a vacuum and heating the product for eight hours at about 180° in a vacuum, or at about $230^\circ/\text{atm.}$, has b. p. $168^\circ/12 \text{ mm.}$, $D_4^{20} 1.0329$, $n_D^{20} 1.5072$, and is insoluble in alkali hydrogen sulphite. Its formula is probably

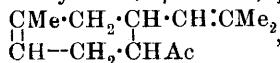


It is hydrolysed by boiling concentrated aqueous potassium hydroxide, yielding β - ψ -citrylideneacetoacetic acid, probably



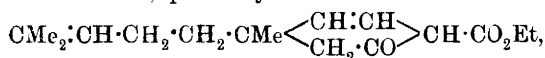
crystals, m. p. 138° (decomp.), which by esterification by alcohol and 25% sulphuric acid at about 60° yields *ethyl β-ψ-citrylideneacetoacetate*, $\text{C}_{16}\text{H}_{24}\text{O}_3$, crystals, m. p. $99\text{---}100^\circ$, from which the β - ψ -acid is regenerated by hydrolysis. By oxidation with alkaline 1% permanganate (6 atoms of oxygen) below 5° , the β - ψ -acid yields an unsaturated acid, $\text{C}_8\text{H}_{12}\text{O}_3$, probably γ -methyl- Δ^{β} -butenylpyruvic

[ϵ -methyl- Δ^8 -hepten- α -onoic] acid, $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CO}_2\text{H}$, needles, m. p. 192° (decomp.), which reduces warm ammoniacal silver oxide solution. By heating above its m. p., the β - ψ -acid loses carbon dioxide and yields β - ψ -ionone, probably

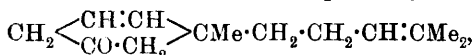


b. p. $125^\circ/19$ mm., D_4^{17} 0.9594, D_4^{22} 0.9547, n_D^{17} 1.49785 (*semi-carbazone*, m. p. 152°).

The β -ester forms a *hydrobromide*, $\text{C}_{16}\text{H}_{25}\text{O}_3\text{Br}$, crystals, m. p. $93-94^\circ$, and is converted by heating with zinc chloride at 180° into β -ionene, $\text{C}_{13}\text{H}_{18}$, an oil with a characteristic odour, b. p. $63^\circ/12$ mm., D_4^{20} 0.8619, n_D^{20} 1.4904. The preceding hydrobromide is converted by boiling aqueous sodium carbonate into *ethyl β -isocitrylideneacetoacetate*, probably

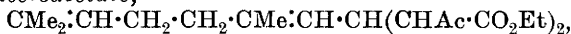


b. p. $160-161^\circ/12$ mm., D_4^{20} 1.0397, n_D^{20} 1.5082, which is insoluble in alkali hydrogen sulphite, regenerates the preceding hydrobromide, and by hydrolysis with boiling concentrated potassium hydroxide solution yields β -isocitrylideneacetoacetic acid, $\text{C}_{14}\text{H}_{20}\text{O}_3$, colourless crystals, m. p. 153° . This acid, the silver salt of which reacts with ethyl iodide to form the β -isoester, is converted by heating at about 160° into β -isoionone, probably



b. p. $113^\circ/15$ mm., D_4^{20} 0.9481, n_D^{20} 1.4929, which forms a *semi-carbazone*, crystals, m. p. 108° , and *p*-bromophenylhydrazone, crystals, m. p. $150-152^\circ$.

The reaction between citral and ethyl acetoacetate (2 mols.) below 0° in the presence of a little piperidine yields *ethyl citrylidenebisacetoacetate*,

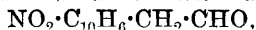


colourless crystals, m. p. 64° , which forms an *oxime*, $\text{C}_{22}\text{H}_{35}\text{O}_6\text{N}$, crystals, m. p. 164° , and is converted by boiling alcoholic potassium hydroxide into 1-methyl-5- β - ζ -dimethyl- Δ^{ac} -heptadienyl- Δ^1 -cyclohexen-3-one, $\text{C}_9\text{H}_{15}\cdot\text{CH}\left\langle\begin{array}{c} \text{CH}_2-\text{CO} \\ \text{CH}_2\cdot\text{CMe} \end{array}\right\rangle\text{CH}$, b. p. $197-198^\circ/15$ mm., D_4^{20} 0.933, $D_4^{16.5}$ 0.932, n_D^{20} 1.50846. The last compound is reduced by sodium and warm alcohol to the corresponding cyclohexanol, $\text{C}_{16}\text{H}_{28}\text{O}$, b. p. $163-164^\circ/11$ mm., $D_4^{18.5}$ 0.900, $n_D^{18.5}$ 1.49182, which is oxidised by chromic acid to the corresponding cyclohexanone, $\text{C}_{16}\text{H}_{26}\text{O}$, b. p. $172^\circ/15$ mm., $D_4^{18.5}$ 0.907, $n_D^{18.5}$ 1.49163, and is converted by phosphoric oxide at 190° into the cyclohexene, $\text{C}_{16}\text{H}_{26}$, b. p. $143-144^\circ/15$ mm., $D_4^{18.5}$ 0.923, $n_D^{18.5}$ 1.4988. C. S.

Naphthylacetic Acids. III. 1-Nitro- β -naphthylpyruvic Acid and 1-Nitro- β -naphthylacetic Acid. FRITZ MAYER and TRUDI OPPENHEIMER (*Ber.*, 1918, 51, 1239-1245. Compare A., 1918, i, 339).—1-Nitro- β -naphthylpyruvic acid is oxidised by

alkaline potassium permanganate to 1-nitro- β -naphthaldehyde, leaflets, m. p. 99° (small yield), and a *nitronaphthoic acid*, m. p. 239° , which is not identical with any of those described by Ekkestrand in 1885. The acid, which is also obtained by oxidising 1-nitro- β -naphthylpyruvic acid by bromine in alkaline solution, yields Friedländer and Littner's 1-amino- β -naphthoic acid, m. p. $202\text{--}205^\circ$, by reduction with ferrous sulphate and hot aqueous ammonia.

1-Nitro- β -naphthylpyruvic acid is reduced to α -naphthindole-2-carboxylic acid, m. p. 213° (Schlieper gives 202°), by ferrous sulphate and aqueous ammonia or by sodium amalgam, and is converted by hot dilute hydrochloric acid and sodium nitrite (1 mol.) into a substance, m. p. 131° , which appears to be 1-nitro- β -naphthylacetoneitrile, $\text{NO}_2\cdot\text{C}_{10}\text{H}_7\cdot\text{CH}_2\cdot\text{CN}$. By treatment with dilute aqueous sodium hydroxide and subsequent distillation with steam, 1-nitro- β -naphthylpyruvic acid yields, in addition to a little nitromethylnaphthalene, a substance the bisulphite compound of which gives α -naphthisatin when decomposed by boiling dilute sulphuric acid, and 1-nitro- β -naphthylacetaldehyde,

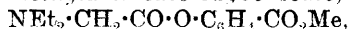


m. p. 212° , by treatment with dilute sulphuric acid in the cold. The last substance reacts with phenylhydrazine to form a *phenylhydrazone*, m. p. 162° , which appears to have the formula $\text{NO}_2\cdot\text{C}_{10}\text{H}_7\cdot\text{CH}(\text{OH})\cdot\text{CH}:\text{N}\cdot\text{NHPh}$, since it contains an additional atom of oxygen.

1-Nitro- β -naphthylacetic acid is reduced to α -naphthoxindole by ferrous sulphate and aqueous ammonia. C. S.

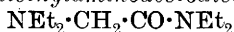
Synthesis of Derivatives of Diethylaminoacetylsalicylic [o-Diethylaminoacetoxybenzoic] Acid. FRIEDRICH L. HAHN and MILLY LOOS (*Ber.*, 1918, 51, 1436—1447).—The following compounds have been prepared partly to obtain substances possessing certain advantages over aspirin and partly to ascertain how the presence of substituents in the acetoxy-group affects the stability of this group. With regard to the second point, the stability appears to be increased by substituents which weaken the acidity of the acetyl group.

Methyl o-chloroacetoxybenzoate, $\text{CH}_3\text{Cl}\cdot\text{CO}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$, m. p. 62° , b. p. $195\text{--}200^\circ/30$ mm., prepared from methyl salicylate, chloroacetyl chloride, and dimethylaniline in the cold, is converted by sodium iodide in acetone solution into the corresponding *iodo*-compound, which in cold ethereal solution reacts with diethylamine to form, after treatment of the product in ethyl acetate solution with hydrogen chloride (not an excess), the *hydrochloride*, m. p. 131° , of *methyl o-diethylaminoacetoxybenzoate*,



crystals, m. p. $58\text{--}59^\circ$ (*picrate*, crystals, m. p. 147°). The *ethyl ester*, $\text{C}_{15}\text{H}_{21}\text{O}_4\text{N}$, b. p. $136\text{--}146^\circ/11$ mm., prepared from *ethyl o-chloroacetoxybenzoate*, m. p. 67° , b. p. $130^\circ/25$ mm., forms a *picrate*, needles, m. p. 138° , and *platinichloride*, m. p. $161\text{--}162^\circ$.

Diethylamine reacts with methyl *o*-chloroacetoxybenzoate to form methyl salicylate and *diethylaminoacetodiethylamide*,



(*picrate*, crystals, m. p. 133°), and with chloroacetyl chloride in ether at 0° to form *chloroacetodiethylamide*, $\text{CH}_2\text{Cl} \cdot \text{CO} \cdot \text{NEt}_2$, b. p. $190\text{--}195^\circ/25$ mm. The last compound is converted into the corresponding *iodo*-compound, which reacts with ethereal diethylamine to form diethylaminoacetodiethylamide.

o-Chloroacetoxybenzoyl chloride, m. p. 55° , b. p. $165\text{--}170^\circ/12$ mm., prepared from the acid and phosphorus pentachloride and phosphoryl chloride, is converted into the *anilide*, m. p. 121° , and the latter into *o*-iodoacetoxybenzanilide, colourless crystals, m. p. 128° , which reacts with diethylamine in ethyl acetate solution to form *o*-diethylaminoacetoxybenzanilide, m. p. $129\text{--}130^\circ$ (*hydrochloride*, m. p. $131\text{--}133^\circ$).

o-Chloroacetoxybenzamide, colourless needles, m. p. 160° , is obtained from *o*-chloroacetoxybenzoyl chloride and ammonium carbonate or ethereal ammonia, or from salicylamide and chloroacetyl chloride in the presence of dimethylaniline. *o*-chloroacetoxybenzochloroacetamide, $\text{CH}_2\text{Cl} \cdot \text{CO} \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_2\text{Cl}$, colourless needles, m. p. $133\text{--}134^\circ$, being an intermediate product in the last method of preparation. *o*-Iodoacetoxybenzamide has decomp. $138\text{--}139^\circ$.

o-Diethylaminoacetoxybenzamide, crystals containing $\frac{1}{2}\text{H}_2\text{O}$, m. p. $144\text{--}145^\circ$, forms a *hydrochloride*, m. p. $195\text{--}196^\circ$, which reacts with sodium nitrite in cold concentrated aqueous solution to form a substance, m. p. about 110° , which is apparently the impure *nitrite*.
C. S.

Reduction of Methyl Formylphenylacetate to Methyl Tropate. WILHELM WISLICENUS and ERNST A. BILHUBER (*Ber.*, 1918, **51**, 1237—1238).—An ethereal solution of methyl formylphenylacetate is reduced by aluminium amalgam and water (compare Müller, A., 1918, i, 223), whereby *methyl tropate*, $\text{C}_{10}\text{H}_{12}\text{O}_3$, colourless needles, m. p. $36.5\text{--}37.5^\circ$, b. p. $159\text{--}162^\circ/19$ mm., is obtained, which yields tropic acid, m. p. $117\text{--}118^\circ$, by hydrolysis.
C. S.

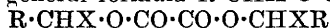
Action of Phosphorus Pentachloride on Formylphenylacetic Ester. WILHELM WISLICENUS and ERNST A. BILHUBER (*Ber.*, 1918, **51**, 1366—1371).—Börner (*Diss.*, Würzburg, 1899) and Koltzscharsch (*Diss.*, Würzburg, 1901) have shown that ethyl formylphenylacetate (liquid α -ester) behaves as a true aldehyde, not as a hydroxymethylene compound, towards phosphorus pentachloride, yielding impure ethyl $\beta\beta$ -dichloro- α -phenylpropionate. A purer product is obtained from the α -methyl ester *Methyl $\beta\beta$ -dichloro- α -phenylpropionate*, $\text{CHCl}_2 \cdot \text{CHPh} \cdot \text{CO}_2\text{Me}$, has b. p. $137\text{--}141^\circ/23$ mm., yields β -chloro- α -phenylacrylic (chloroatropic) acid by boiling with water, and is converted by alcoholic sodium methoxide into *methyl $\beta\beta$ -dimethoxy- α -phenylpropionate*, $\text{C}_{12}\text{H}_{12}\text{O}_4$, m. p. $46\text{--}47^\circ$, b. p. $135\text{--}142^\circ/13$ mm.
C. S.

Studies in the Phenylsuccinic Acid Series. VII. The Action of Alcohols and Amines on *r*-Diphenylsuccinic Anhydride. HENRY WREN and HOWELL WILLIAMS (T., 1918, 113, 832—840).

Preparation of a Calcium Tannate Sparingly Soluble in Dilute Acids. KNOLL & Co. (D.R.-P. 306979 and 307857; from *Chem. Zentr.*, 1918, ii, 494, 694).—If basic calcium tannate is heated for some time at a high temperature, it becomes sparingly soluble in dilute acids; a preparation which had been heated for six hours at 140—150° had the composition $\text{Ca}(\text{OH})\text{C}_{14}\text{H}_9\text{O}_4$, and is recommended for treatment of dysentery.

The modification described in the second patent consists in heating solutions of tannic acid with the quantity of calcium hydroxide necessary for the production of the desired basic salt until the requisite sparing solubility of the basic calcium tannate in dilute acids is attained. H. W.

The Reaction between Acid Haloids and Aldehydes. ROGER ADAMS and E. H. VOLLWEILER (*J. Amer. Chem. Soc.*, 1918, 40, 1732—1746).—The action of benzoyl bromide, of benzoyl chloride and a number of its substitution products, and of oxalyl bromide on aromatic aldehydes has been studied. The general method was to allow the mixtures to remain at the ordinary temperature until solidification occurred, a solvent, however, being occasionally used, more particularly in conjunction with oxalyl bromide. The substances obtained proved to be halogen-substituted esters of the general formula $\text{R}\cdot\text{CHX}\cdot\text{O}\cdot\text{COR}$, or



if oxalyl haloids had been used. They are all decomposed by water into aldehyde, organic acid, and halogen acid, but the difference in the rate of decomposition is very marked; thus, the compound from benzoyl bromide and anisaldehyde decomposes within a few seconds in moist air, whilst the nitrobenzoyl chlorides form compounds which are stable for a long time in cold water. The further reactions and the constitution of these compounds have been studied mainly at the instance of α -bromobenzyl benzoate (from benzoyl bromide and benzaldehyde). This compound is slowly decomposed by cold alcohol, yielding benzaldehyde, hydrogen bromide, and ethyl benzoate, and by an ethereal solution of ammonia, giving benzamide, benzaldehyde, and ammonium bromide; with aniline in dry ethereal solution, it yields α -bromobenzylaniline and benzoic acid. Its constitution follows from its conversion into benzylidene dibenzoate by the action of silver benzoate.

Benzoyl bromide has been condensed with the following aldehydes, the m. p.'s of the *products* being placed within brackets: *o*-bromobenzaldehyde (106—107°); *n*-bromobenzaldehyde (110°); nitroanisaldehyde (101—102°); acetylvanillin (102—103°); *p*-nitrobenzaldehyde (89—90°); bromopiperonal (108—113°); with

vanillin or salicylaldehyde, a vigorous action occurred, but the hydroxy-group was attacked; anisaldehyde (oily); with terephthalaldehyde, a pure product was not obtained; with piperonal, methylsalicylaldehyde, and methylvanillin the products were too unstable to permit purification.

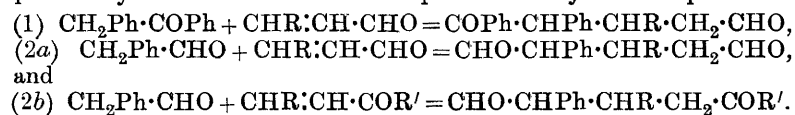
Bromovanillin methyl ether and bromopiperonal react with benzoyl chloride, yielding *substances*, m. p.'s 158—160° and 97—102° respectively, whilst the crystals from benzaldehyde and *o*-, *m*-, and *p*-nitrobenzoyl chlorides have the respective m. p.'s 81—82°, 87—88°, 118—118·5°. Solid substances could not be obtained from benzaldehyde and *p*-chlorobenzoyl chloride, *p*-bromobenzoyl bromide, or *o*-bromobenzoyl chloride.

Oxalyl bromide has been allowed to react with the following aldehydes: benzaldehyde (130—131°); *o*-bromobenzaldehyde (140°); cinnamaldehyde (85—86°); anisaldehyde (ca 66° [decomp.]); nitroanisaldehyde (116—118°); *m*-nitrobenzaldehyde (128—129°); piperonal (81—83°); vanillin (93—95°); acetylvanillin (142—143°); furfuraldehyde (76—77°). Reaction was not observed with *p*-nitrobenzaldehyde.

α -Bromobenzyl benzoate yielded benzylidene dibenzoate, m. p. 62—63°, with silver benzoate, and *benzylidene acetate benzoate*, m. p. 71—72°, with silver acetate; similarly, *benzylidene benzoate p-nitrobenzoate*, m. p. 65—67°, was prepared from α -chloro-*p*-nitrobenzyl benzoate and silver benzoate.

α -Bromobenzyl benzoate reacted with *o*-toluidine in the same manner as with aniline, yielding *benzylidene-o-toluidine*, b. p. 210—212°/72 mm. With dimethylaniline, much heat was developed and a green, resinous product resulted. H. W.

$\alpha\epsilon$ -Dialdehydes and $\alpha\epsilon$ -Keto-aldehydes and their Conversion into ϑ -Lactones. Constitution and Method of Formation of Amaric Acid, Diethylcarbобензоніс Acid and Allied Compounds. HANS MEERWEIN (*J. pr. Chem.*, 1918, [ii], 97, 225—287).— $\alpha\epsilon$ -Dialdehydes and $\alpha\epsilon$ -keto-aldehydes, of which glutardialdehyde is the only member hitherto known, are easily prepared by the two methods represented by the equations:



Method (1) is new, and noteworthy in that it has hitherto been regarded as impossible to effect the addition of a compound containing a reactive methylene group at the double linking of an $\alpha\beta$ -unsaturated aldehyde; yet in some cases the reaction proceeds with astonishing ease (see below). Satisfactory yields of the additive products are obtained by method (2), despite the well-known sensitiveness of phenylacetaldehyde towards alkali; the conclusion must therefore be drawn that the aldehydo-group causes a greater activation of the methylene hydrogen than does the acetyl or carboalkyloxy-group.

The constitutions of the keto-aldehydes described below are proved by oxidising the substances to the δ -ketonic acids, and all of them except ethyl α -acetyl- γ -aldehydo- β - γ -diphenylbutyrate are converted by alcoholic sodium ethoxide into isomeric δ -lactones by an intramolecular Cannizzaro reaction. The stability of the δ -lactones and of the δ -hydroxy-acids obtained from them differs greatly. The α -mono- and $\alpha\alpha$ -di-alkylated δ -hydroxy-acids are the most stable and lactonise comparatively slowly, and the fission of the corresponding lactones is the most difficult. The lactones almost without exception occur in stereoisomeric forms, which are very easily converted one into another by acids and alkalis. Three of the lactones prove to be the long-known diethylcarbобензоник acid, dipropylcarbобензоник acid, and amaric anhydride, and the mechanism of the formation of these substances is now readily explicable.

The type of additive reaction represented in method (1) suggests a new explanation of the formation of benzanthrone from anthrone, glycerol, and sulphuric acid, depending on the structural similarity of anthrone and deoxybenzoin. Aeraldehyde is formed, and this reacts additively with anthrone, producing β -anthronylpropionaldehyde, which passes through dihydrobenzanthrone to benzanthrone.

[With Jos. KLINZ.]— *β -Phenyl- β -desylpropaldehyde,*
 $\text{COPh}\cdot\text{CHPh}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CHO},$

needles, m. p. $176\cdot5$ — 177° (when heated slowly, decomp.), obtained with the development of heat by the addition of 1—2 c.c. of concentrated sodium methoxide solution or pyridine or diethylamine to a solution of equal molecular quantities of cinamaldehyde and deoxybenzoin in methyl alcohol at about 5° , yields β -phenyl- β -desylpropionic (Klingemann's β -dehydroamaric, A., 1893, 589) acid by oxidation with chromic or nitric and glacial acetic acids, and is converted into $\beta\gamma\delta$ -triphenylvalerolactone (Zinin's amaric anhydride) by boiling anhydrous sodium methoxide solution, and into δ -hydroxy- $\beta\gamma\delta$ -triphenylvaleric (α -amaric) acid by aqueous methyl-alcoholic potassium hydroxide at the ordinary temperature, more rapidly by warming. The constitution of β -phenyl- β -desylpropionic acid has been proved by its synthesis. Methyl benzylidenemalonate and deoxybenzoin, condensed as above, yield the additive compound, $\text{COPh}\cdot\text{CHPh}\cdot\text{CHPh}\cdot\text{CH}(\text{CO}_2\text{Me})_2$, needles, m. p. $182\cdot5$ — 183° , which by hydrolysis and loss of carbon dioxide is converted into β -phenyl- β -desylpropionic acid, m. p. 240 — 241° . Klingemann's dehydroamaric anhydride is accordingly the lactone, $\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}$
 $\text{CPh}\cdot\text{CPh}-\text{O}$.

The reduction of β -phenyl- β -desylpropionic acid by sodium amalgam yields an acid which changes very readily into β -amarolactone, $\text{C}_{23}\text{H}_{20}\text{O}_2$, prismatic needles, m. p. 168 — 170° , from which β -amaric acid, $\text{C}_{23}\text{H}_{22}\text{O}_3$, needles (reconverted into the lactone at 156°), is obtained in the usual way. Since β -amaric acid regenerates β -phenyl- β -desylpropionic acid by oxidation, the α - and β -amaric acids are stereoisomerides.

The substance, $C_{11}H_{18}O_2$, m. p. 168° , obtained by Klingemann by heating α -amarolactone (amaric anhydride) with 25% alcoholic sulphuric acid at 100° (*loc. cit.*), is now found to be a third isomeride, $C_{23}H_{20}O_2$, m. p. 171 – 172° , which is named γ -amarolactone. By oxidation with chromic and acetic acids, it yields an isomeric β -phenyl- β -desylpropionic acid, needles, m. p. 173° , which is much more soluble than the acid, m. p. 240 – 241° , is converted into this by fusion, and is identical with Klingemann's α -dehydro-amaric acid.

The additive compound of deoxybenzoin and α -methyl- β -ethylacraldehyde is an oil, which doubtless consists essentially of β -desyl- α -methylvaleraldehyde, $COPh \cdot CHPh \cdot CHEt \cdot CHMe \cdot CHO$, since it yields β -desyl- α -methyl-*n*-valeric acid, m. p. 141.5 – 143° , by oxidation. It has not been obtained crystalline, and decomposes completely by distillation in a vacuum. By treatment in concentrated methyl-alcoholic solution at 30 – 40° with a few c.c. of sodium methoxide solution, it is converted into $\gamma\delta$ -diphenyl- α -methyl- β -ethylvalerolactone, m. p. 152° , which is identical with Zagoumenny's dipropylcarbобензоник acid. The corresponding *hydroxy-acid*, $C_{20}H_{24}O_3$, forms prismatic needles, m. p. 136 – 137° (decomp.). Zagoumenny's dipropylcarbобензоник acid, m. p. 139° , is shown to be a mixture of the β -acid, m. p. 92 – 93° , and the preceding acid, m. p. 152° , which is called the α -acid. The α -acid is converted into the β -acid by heating with methyl-alcoholic potassium hydroxide at 160° for five hours. The β -acid is dimorphous, crystallising also in needles, m. p. 95 – 96° . By oxidation with chromic and acetic acids, the α - and β -acids yield respectively β -desyl- α -methyl-*n*-valeric acid and an isomeric acid, $C_{20}H_{22}O_3$, prismatic needles, m. p. 184.5 – 185° . A third isomeride, needles, m. p. 169 – 171° , is obtained by acidifying a solution of the sodium salt, leaflets, of the β -desyl- α -methyl-*n*-valeric acid, m. p. 141.5 – 143° . By reduction with sodium amalgam, the acid, m. p. 141.5 – 143° , yields, not α -dipropylcarbобензоник acid, but a mixture of two other stereoisomerides, γ -dipropylcarbобензоник acid [γ -($\gamma\delta$ -diphenyl- α -methyl- β -ethylvalerolactone)], needles, m. p. 82 – 84° , and δ -dipropylcarbобензоник acid [δ -($\gamma\delta$ -diphenyl- α -methyl- β -ethylvalerolactone)], needles, m. p. 134° , softening at 130° , of which the latter is insoluble in light petroleum.

The additive compound of crotonaldehyde and deoxybenzoin is β -desylbutaldehyde, $COPh \cdot CHPh \cdot CHMe \cdot CH_2 \cdot CHO$, which yields β -desyl-*n*-butyric acid, needles, m. p. 134 – 136° , by oxidation. The latter is converted into an isomeride, m. p. 153.5 – 154.5° , by 2% aqueous sodium hydroxide at 50 – 60° . A synthesis of β -desylbutyric acid, m. p. 134 – 136° , from deoxybenzoin and ethylidenemalonate ester, analogous to that of β -phenyl- β -desylpropionic acid (above), is described. β -Desylbutaldehyde in methyl-alcoholic solution is transformed by aqueous potassium hydroxide into $\gamma\delta$ -diphenyl- β -methylvalerolactone, m. p. 103 – 104° , which is identical with Zagoumenny's diethylcarbобензоник acid (the α -acid). By oxidation with chromic and acetic acids, the α -acid

yields β -desyl-*n*-butyric acid, m. p. 134—136°, but the latter on reduction yields β -diethylcarbобензоник acid [(β)- $\gamma\delta$ -diphenyl- β -methylvalerolactone], needles, m. p. 144—146°. The oxidation of the β -acid yields the β -desyl-*n*-butyric acid, m. p. 153·5—154·5°, from which it would appear that the β -acid is formed by the reduction (by sodium amalgam), not of the β -desyl-*n*-butyric acid, m. p. 134—136°, but of the isomeric acid, m. p. 153·5—154·5°, so easily obtained from it by the action of alkali hydroxide.

Deoxybenzoin and acraldehyde react additively in methyl-alcoholic solution containing a little sodium methoxide to form β -desylpropaldehyde, which yields β -desylpropionic acid by oxidation. The aldehyde cannot be transformed by alkali into $\gamma\delta$ -diphenylvalerolactone, $C_{17}H_{16}O_2$, needles, m. p. 113—114°, which is obtained, however, by the reduction of β -desylpropionic acid by sodium amalgam.

[With HANS DOTR.]—The additive reaction between phenylacetaldehyde and cinnamaldehyde in cold methyl-alcoholic sodium methoxide solution yields $\alpha\beta$ -diphenylglutardialdehyde. This has not been isolated from the solution, but converted by heating on the water-bath into $\beta\gamma$ -diphenylvalerolactone, prisms or needles, m. p. 123—123·5°, together with a small quantity of a substance, m. p. 134—136°, leaflets, which is possibly $\alpha\beta$ -diphenylvalerolactone. By oxidation with alkaline permanganate, $\beta\gamma$ -diphenylvalerolactone yields $\alpha\beta$ -diphenylglutaric acid, prisms, m. p. 203—204° (methyl ester, needles, m. p. 84—85°), which is converted by prolonged fusion into a stereoisomeride (methyl ester, prisms, m. p. 143°), m. p. between 215° and 232°, according to the rate of heating. For this isomeride Borsche found m. p. 230—231° (A., 1910, i, 35), and Avery and McDole m. p. 223—224° (A., 1908, i, 343). By reduction with hydriodic acid (D 1·7) and red phosphorus at 170°, $\beta\gamma$ -diphenylvalerolactone yields $\beta\gamma$ -diphenyl-*n*-valeric acid, prismatic needles, m. p. 109°, the constitution of which follows by exclusion, since the acid is not identical with either of the stereoisomeric forms of $\alpha\beta$ -diphenylvaleric acid.

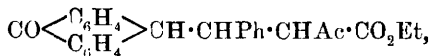
δ -Keto- $\alpha\beta\delta$ -triphenyl-*n*-valeraldehyde, obtained additively from phenylacetaldehyde and phenyl styryl ketone, has also not been isolated, but has been converted through $\alpha\beta\delta$ -triphenylvalerolactone into δ -hydroxy- $\alpha\beta\delta$ -triphenylvaleric acid, needles, m. p. 143—143·5°, which is a remarkably stable acid, but is converted into $\alpha\beta\delta$ -triphenylvalerolactone, needles, m. p. 138—139°, by heating in a vacuum at 150°. The acid is oxidised by chromic acid or potassium permanganate, although not smoothly, to δ -keto- $\alpha\beta\delta$ -triphenylvaleric acid, which is best isolated as the methyl ester, $C_{24}H_{22}O_3$, needles, m. p. 157—158°. The acid, felted needles, m. p. 186—187°, has been obtained by hydrolysing the ester and also synthetically from phenyl styryl ketone and methyl phenylacetate. A second isomeric acid is also obtained by the synthetic method, which has m. p. 260—261°, forms a methyl ester, needles, m. p. 177—178°, and is also obtained by heating the acid, m. p. 186—

187°, at 200—220°. $\alpha\beta\delta$ -Triphenylvalerolactone is reduced to $\alpha\beta\delta$ -triphenylvaleric acid, m. p. 174—175°, by hydriodic acid (D 1·7) and red phosphorus at 170°, and is converted by warm glacial acetic acid containing 10% of sulphuric acid into a *stereoisomeride*, $C_{23}H_{20}O_2$, prisms with $1C_2H_4O_2$, m. p. 124° (174° after removal of acetic acid), from which is obtained a δ -hydroxy- $\alpha\beta\delta$ -triphenylvaleric acid, prisms with 1EtOH, m. p. 155° (not sharp), with reconversion into the lactone.

Phenylacetaldehyde and ethyl benzylideneacetoacetate react additively in alcoholic solution at 5° in the presence of a little sodium ethoxide to form δ -keto- γ -carbethoxy- $\alpha\beta$ -diphenylhexaldehyde, $CHO \cdot CHPh \cdot CHPh \cdot CHAc \cdot CO_2Et$, rhombic leaflets containing $1H_2O$, m. p. 149° (decomp.), and a substance, $C_{23}H_{28}O_5$, prisms, m. p. 79—81°. This substance, the constitution of which has not yet been determined, is also formed by treating the aldehyde with 5% alcoholic hydrogen chloride; it is converted by distillation in a vacuum into an unsaturated substance, $C_{23}H_{26}O_4$, needles, m. p. 129—130°. The preceding aldehyde, which is a viscous oil in the anhydrous state, is converted by distillation in a vacuum into ethyl acetoacetate and α -phenylcinnamaldehyde, crystals, m. p. 94° (oxime, leaflets, m. p. 165—166°; phenylhydrazone, yellow needles, m. p. 125—126°), which has also been synthesised from phenylacetaldehyde and benzaldehyde by Claisen's method.

[With Jos. KLINZ.]—Methyl β -anthronyl- β -phenylisossuccinate, $CO \langle \begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix} \rangle CH \cdot CHPh \cdot CH(CO_2Me)_2$, prisms, m. p. 147°, prepared by adding a few drops of piperidine or diethylamine to a warm methyl-alcoholic solution of anthrone and methyl benzylidene-malonate, is converted into β -anthronyl- β -phenylpropionic acid, prisms, m. p. 195—197° (rapidly heated; decomp. by slow heating), by hydrolysis with boiling 30% sulphuric and glacial acetic acids for four to five days.

By similar additive reactions, anthrone unites with ethyl benzylideneacetoacetate and with phenyl styryl ketone to form ethyl α -acetyl- β -anthronyl- β -phenylpropionate,



needles, m. p. 148—149°, and phenyl β -anthronyl- β -phenylethyl ketone, $CO \langle \begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix} \rangle CH \cdot CHPh \cdot CH_2 \cdot CPh$, needles, m. p. 115—116°, respectively.

C. S.

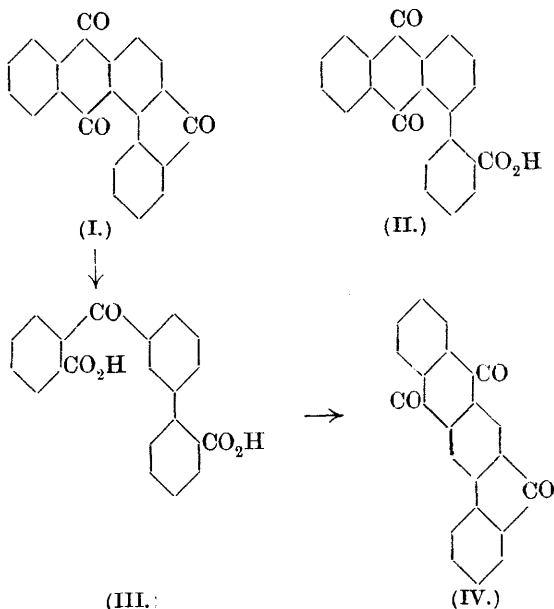
Action of Potassium Ferricyanide on Alizarin in Alkaline Solution and Constitution of Salts of Hydroxyanthraquinones. ROLAND SCHOLL and A. ZINKE (*Ber.*, 1918, **51**, 1419—1435).—By oxidation with an aqueous solution of potassium

ferricyanide and potassium hydroxide at the ordinary temperature, alizarin is converted into an *acid*, $C_{14}H_8O_6$, hydrated, yellow leaflets, m. p. about 230° (decomp.; darkening above 150°), which is purified through the *calcium* salt, and the *monoethyl* ester, yellow or brownish-yellow crystals, m. p. 149° , or *diethyl* esters, yellow plates, prisms, or needles, m. p. $85.5-87^\circ$, and yellow, prismatic needles, m. p. 188° (probably *cis-trans*-isomerides). The acid is shown to be 2-hydroxy-1:4-naphthaquinone-3-vinylglyoxylic acid, $OH \cdot C_{10}H_4O_2 \cdot CH:CH \cdot CO \cdot CO_2H$, by the following evidence. It acts as a dibasic acid, forming a calcium salt, $C_{14}H_6O_6Ca$, which exists in four forms, violet-brown crystals with $7H_2O$, blackish-violet crystals with $3H_2O$, blackish-violet salt with $1H_2O$, and bronze, rhombic leaflets with $2H_2O$, and a *dipotassium* salt, $C_{14}H_6O_6K_2$, brown crystals with $2H_2O$. It forms a vat with alkaline hyposulphite, and therefore contains a quinone grouping. It can be converted into a naphthafuranquinone, and is therefore a naphthaquinone derivative. The monoethyl ester gives a violet-red coloration with alcoholic ferric chloride. The acid reacts additively with bromine.

The views of Perkin (T., 1899, **75**, 433; 1903, **83**, 129), von Georgievics (A., 1902, i, 635; 1905, i, 447), Werner (A., 1908, i, 440), Pfeiffer (A., 1913, i, 879), and Dimroth (*Annalen*, 1916, **411**, 340) on the constitution of hydroxyanthraquinones in the form of their salts and the nature of mordant dyes are discussed without any very definite conclusion being reached. C. S.

Rearrangement Reactions in the Anthraquinonefluorenone Series. ALFRED SCHAARSCHMIDT and JOHANN HERZENBERG (*Ber.*, 1918, **51**, 1230—1237).—1-Chloroanthraquinone-2-carboxylic acid is converted by boiling with toluene and phosphorus pentachloride into the acid *chloride*, pale yellow needles, a suspension of which in benzene is converted into 1-chloro-2-benzoylanthraquinone, $C_{21}H_{11}O_3Cl$, yellow leaflets, m. p. 196° , by heating with aluminium chloride at 60° for four hours. 1-Amino-2-benzoylanthraquinone, red needles, m. p. 190° , prepared by heating the preceding substance with alcohol and aqueous ammonia at $170-175^\circ$, is diazotised in concentrated sulphuric acid solution at $17-22^\circ$, the solution is poured on to ice so that the temperature does not exceed about 35° , copper powder is added, and the mixture warmed on the water-bath, whereby anthraquinone-2:1-fluorenone (formula I), golden-yellow leaflets (from nitrobenzene), m. p. 317° , is obtained, which forms an intensely red vat with sodium hyposulphite. By fusion with potassium hydroxide at $220-230^\circ$, anthraquinone-2:1-fluorenone is converted, not into 1-o-carboxyphenylanthraquinone (formula II) as might be expected from the behaviour of allochrysoketonecarboxylic acid (Schaarschmidt, A., 1917, i, 274), but into a mixture of acids containing the dicarboxylic acid (formula III), since by treatment with concentrated sulphuric

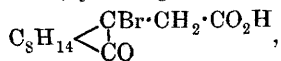
acid, Ullmann and Dasgupta's anthraquinone-2:3-fluorenone (A., 1914, i, 413) was obtained (formula IV).



C. S. .

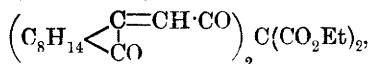
Camphor Ketones. HANS RUPE, MARKUS WARDER, and KUNIHICO TAKAGI (*Helv. Chim. Acta*, 1918, i, 309—342).—The work of Rupe and Iselin (A., 1916, i, 409) and of Rupe and Burckhardt (A., 1917, i, 141) on the preparation of derivatives of methylenecamphor has been extended in several directions, particularly with a view to the preparation of an unsaturated camphor ketone; the optical investigation of the substances is not yet quite completed, and fuller details are promised in a subsequent communication.

Camphorylideneacetic acid, $\text{C}_8\text{H}_{14} \begin{smallmatrix} \text{C}=\text{CH}\cdot\text{CO}_2\text{H} \\ \text{CO} \end{smallmatrix}$, m. p. $99.5-101^\circ$, $[\alpha]_D +182.3^\circ$ in benzene, is prepared by a modification of the method of Bishop, Claisen, and Sinclair (A., 1895, i, 62) [the microcrystalline *magnesium* salt and the ethyl ester, pale yellow, inodorous oil, b. p. $149.5-150^\circ/12$ mm., $D_4^{20} 1.0459$, $[\alpha]_D +170.1^\circ$ (in substance), $+160.4$ (in benzene), are described], and is converted by thionyl chloride into the corresponding *chloride*, m. p. $34-35^\circ$, b. p. $140-141^\circ/13$ mm. The free acid reacts with hydrogen bromide in glacial acetic acid solution, yielding the *bromo-acid*,



long, colourless needles, m. p. 153—154° (decomp.), but the action appears to be balanced, since, at a slightly higher temperature, hydrogen bromide is eliminated with re-formation of camphorylideneacetic acid. The latter substance does not react normally with bromine. *Camphorylacetic acid*, small, prismatic crystals, m. p. 83—84°, b. p. 191·5—192·5°/12 mm., $[\alpha]_D + 38\cdot0$ in benzene, is prepared by reducing camphorylideneacetic acid with sodium amalgam, or, better, with hydrogen, in the presence of nickel; its *ethyl ester* has b. p. 154—155°/10 mm., $[\alpha]_D + 67\cdot5^\circ$ (in substance), $+ 37\cdot1^\circ$ (in benzene). Attempts to reduce camphorylideneacetyl chloride by zinc dust and acetic acid led to the isolation of a mixed *anhydride* of camphorylacetic and acetic acids, $C_8H_{14} \begin{smallmatrix} \diagup \\ \text{C} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{O} \cdot \text{Ac} \\ \diagdown \\ \text{CO} \end{smallmatrix}$, fine needles or transparent plates, m. p. 118—120°.

Ethyl dicamphorylideneacetylmalonate,



pale yellow needles, m. p. 90—91°, is prepared by the condensation of camphorylideneacetyl chloride with ethyl sodiomalonate in ethereal solution (*ethyl dicamphorylideneacetylacetoacetate*, fine needles, m. p. 149—150°, is similarly obtained from ethyl acetoacetate), and is hydrolysed by dilute sulphuric acid in acetic acid solution to *camphorylideneacetone*, $C_8H_{14} \begin{smallmatrix} \diagup \\ \text{C} = \text{CH} \cdot \text{CO} \cdot \text{CH}_3 \\ \diagdown \\ \text{CO} \end{smallmatrix}$, lemon-yellow liquid, b. p. 137—138°/10 mm., $D_4^{20} 1\cdot0327$, $[\alpha]_D + 208\cdot8^\circ$ (in substance), $186\cdot6^\circ$ (in benzene), and camphorylideneacetic acid. The ketone does not appear to yield a stable sodium hydrogen sulphite compound; the *benzylidene* derivative forms golden-yellow needles, m. p. 94—95°, *p-nitrobenzylidene* derivative, lemon-yellow, minute crystals, m. p. 150—151°, *oxime*, colourless, shining needles, m. p. 142—143°, *phenylhydrazone*, orange-yellow needles, m. p. 145—146°, *hydrazone*, long, yellow needles, m. p. 112—113°. With semicarbazide the ketone gives a *compound*, $C_{14}H_{21}O_2N_3$, prismatic needles or small leaflets, decomposing at 223—224°, which does not behave as a normal semicarbazone.

Attempts to prepare *camphorylaceton*e by a similar sequence of actions were less successful. *Camphorylacetyl chloride*, pale yellow, inodorous liquid, b. p. 152—154°/12 mm., could only be condensed with ethyl sodiomalonate with considerable difficulty, giving a small yield of substance, from which by hydrolysis camphorylaceton was obtained in small quantity. The saturated ketone could, however be satisfactorily prepared by reduction of camphorylideneacetone with hydrogen in the presence of nickel, although the camphor carbonyl group was invariably attacked to some extent; after purification through the *semicarbazone*, long needles, m. p. 203—204° (decomp.), it was obtained as an inodorous, highly refractive oil, b. p. 148·5—149°/12 mm., $D_4^{20} 1\cdot0213$, $[\alpha]_D + 49\cdot2^\circ$ (in substance), $+ 60\cdot7^\circ$ (in benzene). The ketone behaves towards sodium hydrogen sulphite in the same manner as the unsaturated ketone; it yields a

phenylhydrazone, needles, m. p. 87—89°, and a *benzylidene* derivative, colourless leaflets, m. p. 75—76°.

The preparation of a camphordiketone is also described, although the yields leave much to be desired in spite of many variations of the experimental conditions; ethyl camphorylacacetate condenses with acetophenone in ethereal solution in the presence of solid sodium ethoxide, giving small amounts of *camphorylacetylacetophenone*, $C_8H_{14} \begin{smallmatrix} \text{CH} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{COPh} \\ \text{CO} \end{smallmatrix}$, m. p. 52—61°, $[\alpha]_D + 62 \cdot 5^\circ$ in

benzene. An alcoholic solution of the diketone gives an immediate bluish-red coloration with ferric chloride. The *copper* salt, long, greyish-green needles, m. p. 184—186°, and *sodium* salt are described. H. W.

Preparation of Camphylcarbinol. HANS RUPE (D.R.-P. 307357; from *Chem. Zentr.*, 1918, ii, 493).—Hydroxymethylenecamphor only suffers reduction at the ethylenic bond when reduced by hydrogen in the presence of finely divided nickel or cobalt in alcoholic, aqueous-alcoholic, or acetic acid solution, or as normal alkali salt in aqueous solution; *camphylcarbinol*, which is thus produced, is a colourless, odourless oil, b. p. 142—143°/10 mm., D_4^{20} 1·0502, $[\alpha]_D^{20} + 62 \cdot 22^\circ$. [See further, following abstract.] H. W.

Reduction Products of Hydroxymethylenecamphor. H. RUPE, A. AKERMANN, and H. TAKAGI (*Helv. Chim. Acta.*, 1918, 1, 452—472).—The reduction of hydroxymethylene compounds by hydrogen in the presence of colloidal palladium or platinum has been studied by Kötze and Schaeffer (A., 1912, i, 603), who found that methyl ketones were formed; hydroxymethylenecamphor, however, was unaffected by this treatment, a result which was attributed to the acidic character of the substance. The authors find that hydroxymethylenecamphor is readily reduced by hydrogen in the presence of a specially prepared nickel catalyst (the mode of procedure is fully described in the original paper and iron and copper are shown to act as poisons). The main product (about 80—95%) of the reaction is *camphylcarbinol*, $C_8H_{14} \begin{smallmatrix} \text{CH} \cdot \text{CH}_2 \cdot \text{OH} \\ \text{CO} \end{smallmatrix}$; it is purified by repeated fractionation under diminished pressure, or, preferably, by means of the calcium chloride compound; the optically pure substance is isolated through the benzoyl derivative (see later). It forms a colourless, odourless, viscous oil, b. p. 139—140°/9 mm., 143—144°/11 mm., D_4^{20} 1·0502, $[\alpha]_D^{20} + 49 \cdot 13^\circ$, $[\alpha]_B^{20} + 65 \cdot 73^\circ$, $[\alpha]_E^{20} + 82 \cdot 44^\circ$, $[\alpha]_F^{20} + 120 \cdot 82^\circ$, $[\alpha]_F/[\alpha]_C$ 2·45°, λ_D 578. With phosphorus tribromide it yields the corresponding *bromide*, long needles, m. p. 65·5—66°, and with hydrogen chloride, or, preferably, thionyl chloride, the corresponding *chloride*, leaflets, m. p. 53—54°, b. p. 125—127°/14 mm. Attempts to convert the alcohol into the aldehyde were unsuccessful; chromic oxide converted it into camphorquinone, m. p. 197°, whilst manganese dioxide and sulphuric

acid gave a small quantity of substance, m. p. 201° , and much unchanged carbinol. Benzoyl chloride in the presence of pyridine converts the carbinol practically quantitatively into the *benzoyl* derivative, colourless, shining plates or prisms, m. p. $95-97^{\circ}$; attempts to hydrolyse the latter with alcoholic potassium hydroxide, with barium hydroxide, or magnesia resulted in the formation of methylenecamphor. Experiments with aqueous alcoholic sulphuric acid were more successful, and from these it was found possible to isolate camphylcarbinol, although dehydration of the latter also occurred to a considerable extent. The *formyl* derivative, long needles, m. p. $74-75^{\circ}$, b. p. $142-143^{\circ}/11$ mm., and the *acetyl* derivative, colourless, mobile oil, b. p. $148.5-149^{\circ}/10$ mm., were prepared by the action of formic acid (86%) and acetic anhydride respectively on the carbinol, but attempts to prepare the hydrogen phthalate led to the production of methylenecamphor.

The by-products of the preparation of camphylcarbinol consist of methylenecamphor, methylcamphor, and the ethyl ethers of camphylcarbinol and hydroxymethylenecamphor. The two substances first named are contained in the first fractions, b. p. *ca.* $82-84^{\circ}/10$ mm., and are separated by converting the methylenecamphor into the hydrobromide (camphylbromomethane), from which it can be re-generated by treatment with methyl-alcoholic potassium hydroxide; the pure substance is, however, more conveniently prepared by heating camphylcarbinol with the same reagent, and then forms a characteristic, waxy mass, m. p. $43.5-44^{\circ}$. It becomes polymerised when repeatedly distilled under diminished pressure. With bromine it yields a *dibromide*, m. p. $108-109^{\circ}$. *Methylcamphor*,

$\text{C}_8\text{H}_{14} \begin{array}{c} \text{CHMe} \\ \diagup \quad \diagdown \\ \text{CO} \end{array}$, can be isolated in an almost pure state by repeated

fractionation of the residues from the methylenecamphor hydrobromide, but is more conveniently obtained by the direct hydrogenation of methylenecamphor in the presence of finely divided nickel; it has m. p. $37.5-38.5^{\circ}$, b. p. $88-89^{\circ}/8.5$ mm. Direct experiment shows the formation of methylenecamphor to be due to the dehydrating action of the nickel catalyst on primarily formed camphylcarbinol.

The ethyl ethers of camphylcarbinol and hydroxymethylenecamphor were not isolated as such; their presence is inferred from the fact that the action of alcoholic potassium hydroxide on the fractions of higher b. p. of the by-products leads to the production of methylenecamphor and hydroxymethylenecamphor respectively; their formation is attributed to the addition of ethyl alcohol to methylenecamphor and to the condensation of hydroxymethylenecamphor and alcohol under the influence of nickel. H. W.

Synthesis of Curcumin. V. LAMPE (*Ber.*, 1918, 51, 1347-1355).—The course of the synthesis is as follows: ethyl α -carbomethoxyferuloylacetate \rightarrow carbomethoxyferuloylacetone \rightarrow dicarbomethoxydiferuloylacetone \rightarrow dicarbomethoxydiferuloylmethane \rightarrow diferuloylmethane (curcumin).

Ethyl α-carbomethoxyferuloylacetoacetate [*ethyl α-4-methylcarbonato-3-methoxycinnamoylacetoacetate*],

$\text{CO}_2\text{Me}\cdot\text{O}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{CHAc}\cdot\text{CO}_2\text{Et}$, obtained by digesting ethyl sodioacetoacetate and carbomethoxyferuloyl [4-methylcarbonato-3-methoxycinnamoyl] chloride in dry ether on the water-bath, forms faintly yellow needles, m. p. 91—93°; a by-product of the reaction is *methyl carbonatomethoxycinnamic anhydride*, $\text{C}_{24}\text{H}_{22}\text{O}_{11}$, colourless leaflets, m. p. 142—144°. *Ethyl α-feruloylacetoacetate*, $\text{C}_{16}\text{H}_{18}\text{O}_6$, canary-yellow, prismatic needles, m. p. 116—118°, is obtained by shaking an ethereal solution of the methyl carbonato-derivative with 1% aqueous sodium hydroxide and treating the alkaline solution with carbon dioxide.

Carbomethoxyferuloylacetone [4-methylcarbonato-3-methoxycinnamoylacetone], $\text{CO}_2\text{Me}\cdot\text{O}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{COMe}$, faintly yellow, prismatic needles, m. p. 111—113°, is obtained by hydrolysing ethyl α-methylcarbonatomethoxycinnamoylacetoacetate, carbon dioxide being also eliminated; it is converted into *feruloylacetone*, $\text{C}_{13}\text{H}_{14}\text{O}_4$, prisms, m. p. 143—145°, by dilute alkali.

A solution of methylcarbonatomethoxycinnamoylacetone in anisole is treated with finely divided sodium, and a day later a solution of methylcarbonatomethoxycinnamoyl chloride in warm anisole is added. The mixture is treated after twenty-four hours with water containing a little hydrochloric acid, and the anisole is removed by distillation with steam. The heavy, dark red residue, probably dimethylcarbonatomethoxydicinnamoylacetone, is boiled with dilute acetic acid, and thus converted into dimethylcarbonatomethoxydicinnamoylmethane, m. p. 145—148—158°; after crystallisation from benzene the substance is pure, has m. p. 170—172°, and is identical with Milobendzka, Kostanecki, and Lampe's dimethylcarbonato-curcumin (A., 1910, i, 628); the last substance has m. p. 170—172° after being crystallised from benzene. On hydrolysis dimethylcarbonatomethoxydicinnamoylmethane yields diferuloylmethane, $\text{CH}_2(\text{CO}\cdot\text{CH}:\text{CH}\cdot\text{C}_6\text{H}_3[\text{OMe}]\cdot\text{OH})_2$, prisms, m. p. 180—183°, which is identical with natural curcumin. C. S.

Synthesis of *pp'*-Dihydroxy- and *p*-Hydroxydicinnamoylmethane. V. LAMPE and M. GODLEWSKA (*Ber.*, 1918, 51, 1355—1360).—The method of synthesising dicinnamoylmethane (Lampe and Milobedzka, A., 1913, i, 876) has been extended to include the hydroxy-derivatives, partly in connexion with the synthesis of curcumin (preceding abstract), partly to obtain substances which are of interest in connexion with the theory of direct dyes.

The condensation of ethyl acetoacetate and *p*-methylcarbonatocinnamoyl chloride in ethereal solution by means of sodium ethoxide yields, in addition to a little *p-methylcarbonatocinnamic anhydride*, $\text{C}_{22}\text{H}_{18}\text{O}_9$, colourless aggregates, m. p. 168—170°, *ethyl α-p-methylcarbonatocinnamoylacetoacetate*,

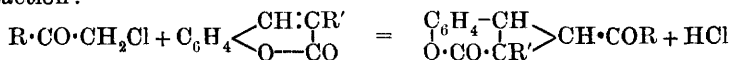
$\text{CO}_2\text{Me}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{CHAc}\cdot\text{CO}_2\text{Et}$, faintly yellow prisms, m. p. 94—96°, which yields by hydrolysis and simultaneous elimination of carbon dioxide *p-methylcarbonatocin-*

namoylacetone, $\text{CO}_2\text{Me}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{COMe}$, faintly yellow leaflets, m. p. 111—113°. The last compound reacts in ethereal solution with very dilute alkali to form *p*-hydroxycinnamoylacetone, yellow leaflets, m. p. 144—146°, in boiling alcoholic solution with hydroxylamine hydrochloride to form 3(or 5)-*p*-methylcarbonatostyryl-5(or 3)-methylisooxazole, $\text{C}_{14}\text{H}_{13}\text{O}_4\text{N}$, colourless leaflets, m. p. 122—124°, and in anisole solution with sodium and *p*-methylcarbonatocinnamoyl chloride to form, after the initial product has been boiled with dilute acetic acid (compare preceding abstract), *pp'*-dimethylcarbonatodicinnamoylmethane, $\text{C}_{23}\text{H}_{20}\text{O}_8$, canary-yellow aggregates, m. p. 162—166°. The last substance reacts with hydroxylamine hydrochloride in alcoholic solution to form 3:5-di-*p*-methylcarbonatostyrylisooxazole, $\text{C}_{23}\text{H}_{19}\text{O}_7\text{N}$, colourless aggregates, m. p. 178—180°, and in ethereal solution with 1% aqueous sodium hydroxide to form *pp'*-dihydroxydicinnamoylmethane, $\text{C}_{19}\text{H}_{16}\text{O}_4$, faintly orange needles, m. p. 218—220° (decomp.).

p-Methylcarbonatodicinnamoylmethane, $\text{C}_{21}\text{H}_{18}\text{O}_5$, yellow needles, m. p. 114—116°, is obtained from cinnamoylacetone and *p*-methylcarbonatocinnamoyl chloride or *p*-methylcarbonatocinnamoylacetone and cinnamoyl chloride by the aid of sodium and acetic acid (as above), and yields by elimination of the carbomethoxy-group *p*-hydroxydicinnamoylmethane, faintly orange, prismatic needles, m. p. 190—192°.

Unmordanted cotton is dyed faintly orange by curcumin, canary-yellow (not fast to soap) by *pp'*-dihydroxydicinnamoylmethane, and faintly yellow by *p*-hydroxydicinnamoylmethane. A similar regularity occurs in the reaction with boric acid, which colours turmeric (curcumin) paper intensely orange, changes the colour of *pp'*-dihydroxydicinnamoylmethane to a weak orange, and does not affect the colour of *p*-hydroxydicinnamoylmethane. C. S.

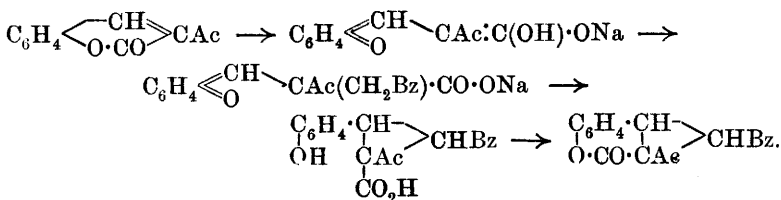
A New Group of cycloPropane Derivatives. III. Scope and Mechanism of the Reaction. Behaviour of 3-Acetylcoumarin with Solutions of Alkali Hydroxides. OSKAR WIDMAN (*Ber.*, 1918, 51, 1210—1214. Compare A., 1918, i, 347, 393).—The formation of the new cyclopropane derivatives by the reaction:



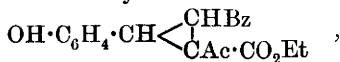
(*loc. cit.*) succeeds when $\text{R}=\text{Ph}$, *o*- or *p*- $\text{C}_6\text{H}_4\cdot\text{OMe}$, $\text{C}_6\text{H}_4\cdot\text{NO}_2$, or C_{10}H_7 and $\text{R}'=\text{Ac}$, COEt , Bz , CO_2Et , CO_2Me , or CN , but fails when $\text{R}=\text{Me}$ and $\text{R}'=\text{Ph}$ or H . The formation also fails when ethyl coumarin-4-carboxylate is used instead of a suitably 3-substituted coumarin. Attempts also failed to bring about, in the presence of sodium ethoxide, a reaction between phenacyl haloids and esters of fumaric, ethylenetetracarboxylic, benzyldieneacetoacetic, benzyldienemalonic, anisylidenemalonic, and *o*-ethoxybenzyldieneacetoacetic acids in such a way that the phenacylidene group is combined at a double linking. It appears, therefore, that only 3-substituted coumarins can enter into the preceding reaction, and even then only

if the substituent is an aliphatic or aromatic acyl group, a carboalkyloxy-group, or a cyano-group.

In seeking to account for the reaction, the author has revised his explanation of the action of alkalis on 3-acetylcoumarin (A., 1902, i, 374). The yellow colour developed with a cold solution of alkali hydroxide is now attributed, not to the formation of 3-hydroxyvinylcoumarin, because 3-trimethylacetyl- and 3-benzoyl-coumarin, in which the formation of the hydroxyvinyl group is impossible, also develop a yellow colour, but to the formation of an orthoquinonoid sodium compound. This reacts with the phenacyl haloid in accordance with the scheme:



When alcoholic sodium ethoxide is used a certain amount of the substance $\text{O}:\text{C}_6\text{H}_4:\text{CH}:\text{CAc}:\text{C}(\text{OEt})\cdot\text{ONa}$ is formed, and this reacts with the phenacyl haloid to yield the coumarinic ester,



and thus is explained the formation of a by-product differing from the main product in containing an additional molecule of ethyl alcohol (*loc. cit.*).
C. S.

A Synthesis of *iso*Brazilein and certain Related Anhydro-pyranol Salts. I. HERBERT GRACE CRABTREE, ROBERT ROBINSON, and MAURICE RUSSELL TURNER (T., 1918, 113, 859—880).

Preparation of Hydrogenated Alkaloids. C. F. BOEHRINGER & SÖHNE (D.R.-P., 307894; additional to D.R.-P., 306939; from *Chem. Zentr.*, 1918, ii, 693—694).—The addition of hydrogen to alkaloids or their salts in the presence of small quantities of the finely divided suboxides of the nickel group (A., 1918, i, 546) at temperatures not exceeding 60° can also be effected in alcoholic suspension or solution. The preparation of dihydroquinine from quinine monohydrochloride and the hydrogenation of cinnamylcocaine are cited as examples.
H. W.

Cinchona Alkaloids. I. Cupreine, Hydrocupreine, and their Methyl and Ethyl Ethers. G. GIEMSA and J. HALBERKANN (*Ber.*, 1918, 51, 1325—1333).—Contrary to the statement of Hesse (A., 1888, 71), dihydrocupreine instantly decolorises potassium permanganate in acid solution. It has m. p. 204° (Hesse gives 168—170°; Pum, 170°), and can readily be obtained by the addition of hydrogen to cupreine in alcoholic solution (palladium catalyst) or to cupreine hydrochloride in aqueous solution (nickel catalyst).

Cupreine yields methylcupreine (quinine) by methylation with methyl sulphate and alkali in methyl-alcoholic solution, or, much better, with ethereal diazomethane in amyl-alcoholic solution.

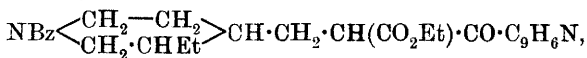
Methyldihydrocupreine, prepared by the catalytic reduction of quinine or the methylation of dihydrocupreine, is isolated as the *basic sulphate*, which contains $6\text{H}_2\text{O}$ and is relatively stable to potassium permanganate. Ethyldihydrocupreine is prepared by similar methods.

C. S.

The Cinchona Alkaloids. XX. Synthesis of Quinotoxines.

PAUL RABE and KARL KINDLER (*Ber.*, 1918, **51**, 1360—1365. Compare A., 1918, i, 303).—The problem of the synthesis of quinotoxines resolves itself into three parts: (1) the synthesis of cinchoninic and 6-methoxycinchoninic acids, (2) the synthesis of homomeroquinene and homocincholeupone, and (3) the condensation of each of the first with each of the second pair to give the four quinotoxines, cinchonidine, dihydrocinchonidine, quinidine, and dihydroquinidine.

The first part will be dealt with in a later communication by Rabe. With regard to the second part, the two substances have not yet been synthesised, and the material used by the authors in realising the third part has been obtained by the fission of quinotoxines. Thus *N*-benzoylhomo-cincholeupone, obtained from benzoyldihydrocinchotoxine by a slight modification of Kaufmann and Brunnschweiler's method (A., 1917, i, 50), is converted into its *ethyl* ester, $\text{C}_{19}\text{H}_{27}\text{O}_3\text{N}$, a viscous oil, b. p. $256^\circ/13$ mm., which yields, after hydrolysis by dilute hydrochloric acid and subsequent re-esterification, *ethyl homocincholeupone*, $\text{C}_{12}\text{H}_{23}\text{O}_2\text{N}$, b. p. $140^\circ/13$ mm. The reaction between ethyl cinchoninate and ethyl *N*-benzoylhomo-cincholeupone in the presence of sodium ethoxide in boiling benzene for fifteen hours leads to a product, doubtless the β -ketonic ester,



which is converted into dihydrocinchotoxine (dihydrocinchonidine) by hydrolysis with boiling 15% hydrochloric acid.

Since dihydrocinchotoxine can be converted into dihydrocinchoninone (A., 1909, i, 253), and the latter has been reduced by aluminium and sodium ethoxide to dihydrocinchonine and dihydrocinchonidine (future communication), therefore the construction of cinchona alkaloids from derivatives of the quinoline and piperidine series has been accomplished.

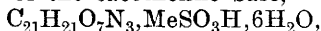
C. S.

Degradation of Scopoline. ERNST SCHMIDT (*Ber.*, 1918, **51**, 1281—1283).—A claim for priority over Hess with respect to the conversion of dihydroscopoline into 1-methylpiperidine-2:6-dicarboxylic acid, and a denial of his statement (A., 1918, i, 404) that the author has asserted that the group $\text{O} \left\langle \begin{array}{c} \text{C}(\text{OH}) \\ \text{CH} \end{array} \right\rangle$ is present in scopoline.

C. S.

Strychnine Alkaloids. XXIV. Cause of the Violet Colour Reaction of Cacotheline and of Nitro-compounds of the Brucine Series Allied to it. HERMANN LEUCHS (*Ber.*, 1918, 51, 1375—1389).—

The action of nitric acid on brucine is represented by the scheme $C_{23}H_{26}O_4N_2 \rightarrow C_{21}H_{20}O_4N_2 \rightarrow C_{21}H_{19}O_6N_3 \rightarrow C_{21}H_{21}O_7N_3, HNO_3$ (A., 1911, i, 746). Cacotheline, the final product, would appear to be a nitrated quinone were it not that sulphurous acid does not produce a less intensely coloured or colourless quinol (A., 1910, i, 1042), but a substance having a deep violet or deep green colour. Brucinolone and isobrucinolone when treated with nitric acid undergo analogous changes (A., 1909, i, 954; 1912, i, 210; 1913, i, 194), the final product being undoubtedly a nitro-quinone, since it is reduced by sulphurous acid to a pale yellow quinol. Hence by analogy the cacotheline base is a nitro-quinone, despite the objection raised above. The same holds in the case of the methonitrate of the cacotheline base, $C_{21}H_{21}O_7N_3, MeNO_3$, obtained by the action of nitric acid on methylbrucine (A., 1911, i, 1018). The methonitrate also gives a violet coloration with sulphurous acid, but its quinonoid nature is shown first by the reaction with aqueous hydroxylamine hydrochloride, whereby the *oxime*, $C_{22}H_{25}O_7N_4Cl, 2H_2O$, yellow needles, of the methochloride of the cacotheline base is obtained, and, secondly, by reduction by tin and *N*-hydrochloric acid, whereby four atoms of hydrogen are taken up and a *stannichloride*, broad, rectangular prisms, is obtained, $C_{22}H_{28}O_5N_3Cl, HCl, SnCl_4, 6H_2O$, from which the *hydrochloride* of presumably an amino-quinol, $C_{22}H_{28}O_5N_3Cl, HCl, H_2O$, colourless, crystalline powder, decomp. 260° , is prepared. The behaviour of the methonitrate towards sulphurous acid is at variance with the preceding evidence of quinonoid structure. Thus with aqueous sodium hydrogen sulphite it yields, in the cold at 0° , a *methosulphite* of the cacotheline base,



colourless leaflets, which evolves sulphur dioxide on treatment with strong acids, and in the hot solution an isomeric *methosulphite*, deep violet, almost black prisms with metallic lustre (into which the colourless isomeride changes by keeping), which dissolves in concentrated sulphuric acid without evolution of sulphur dioxide, and is precipitated unchanged by the addition of water. Probably, therefore, the sulphurous acid in the violet compound is not only attached to the basic nitrogen atom, but also enters into complex combination with some other portion of the molecule. By treatment with 5*N*-nitric acid, the violet compound loses two atoms of hydrogen and is converted into a *substance*, $C_{21}H_{19}O_7N_3, MeSO_3H$, reddish-yellow leaflets or prisms with $2H_2O$, which appears to bear to the violet compound the relation of quinone to quinol, since it is converted into the latter by sulphurous acid or by nickel and hydrochloric acid. Hydroxylamine, however, converts the reddish-yellow substance into the violet compound in acid solution and into the oxime of the methochloride of the cacotheline base in alkaline solution. The complete reduction of the reddish-yellow

substance by tin and hydrochloric acid yields at first a violet precipitate, and, finally, a *substance*, $C_{22}H_{25}O_7N_3S$, colourless needles, which appears to be the anhydride resulting by the elimination of water from an amino- and the SO_3H -groups. The SO_2 group is still present in complex union in the anhydride, but is eliminated by warm *N*-alkali hydroxide, without, however, definite products being formed.

The violet compound, $C_{21}H_{21}O_7N_3, MeSO_3H$, is stable in aqueous ammonia in the absence of oxygen, but when the latter is admitted is oxidised, to the extent of 10% to the reddish-yellow nitro-quinone methosulphite and to the extent of 60% to a *substance*, $C_{21}H_{23}O_{11}N_3S$, reddish-yellow prisms and polyhedra, carbonising at about $280-290^\circ$.

Apart from their acidic groups, the methonitrate of the cacotheline base, and the violet methosulphite obtained from it by the action of sodium hydrogen sulphite, are isomeric substances. The former is a nitro-quinone and the latter a nitro-quinol. The reduction of the one to the other is not effected at the expense of the sulphurous acid, because the two substances are isomeric. The author is of opinion that intramolecular reduction occurs at the expense of a $\cdot CH(OH) \cdot$ group in the cacotheline base, and that the resulting $\cdot CO \cdot$ group enters into complex union with the sulphite group; thus, (i) $\cdot CO \cdot CO \cdot + \cdot CH \cdot OH \rightarrow \cdot C(OH) : C(OH) \cdot + \cdot CO \cdot$, and (ii) $: NMe \cdot SO_3H + \cdot CO \rightarrow : NMe \cdot SO_2 \cdot O \cdot C(OH) \cdot$. C. S.

Acid Esters of 2 : 6-Dimethylcinchomeronic Acid. RUD. WEGSCHEIDER (*Ber.*, 1918, **51**, 1478—1479).—Mumm and Hüneke's argument that the acid ester produced by the interaction of alcohol and the acid anhydride must be the γ -ester on steric grounds (*A.*, 1918, i, 183) is inadmissible, because the author has shown frequently (1895—1912) that in reactions of this kind the alcohol attacks the strongest carboxyl group present, even though it may be sterically protected. C. S.

New Cases of Isomerism in the Isatin Series. II. GUSTAV HELLER (*Ber.*, 1918, **51**, 1270—1281).—The existence of 5 : 7-dimethylisatin (and also of four dimethyl ethers) in four modifications (*A.*, 1918, i, 235) is now shown to be incorrect. 5 : 7-Dimethylisatin I is the lactam, $C_6H_2Me_2 \begin{smallmatrix} CO \\ \diagup \diagdown \\ NH \end{smallmatrix} \cdot SO$, since it exhibits all the reactions characteristic of isatin itself in the lactam form. The O-silver salt does not exist, the compound previously described as such being a complex substance containing very much more silver than the amount corresponding with the simple formula. The only silver derivative is the N-salt, and this reacts with methyl iodide in the presence of benzene at 100° to form the lactim ether, $C_6H_2Me_2 \begin{smallmatrix} CO \\ \diagup \diagdown \\ N \end{smallmatrix} \gg C \cdot OMe$, m. p. 232° , which is identical with the previously described methyl ether of isomeride II (m. p. erroneously given as 247°). The sodium salt and methyl iodide yield the lactam ether.

Isomeride II.—This is produced from the isomeride I, has the same composition, is unimolecular, gives the indophenin reaction, and yields the preceding lactim ether by warming with methyl sulphate. It is therefore 5:7-dimethylisatin in the lactim form, which, unlike the corresponding form of isatin, is capable of isolated existence.

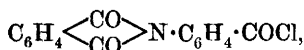
The lactim methyl ether is converted into 5:7-dimethylisatin (lactam) by boiling glacial acetic acid or hot dilute aqueous sodium hydroxide.

Since 5:7-dimethylisatin can exist in the lactam and the lactim forms, its salts may be N- or O-salts. The silver and the sodium salts prepared from the lactam regenerate this on acidification, and are thus N-salts, and therefore by analogy the silver and the sodium salts of isatin itself are lactam salts. No evidence of the formation of O-salts has been obtained.

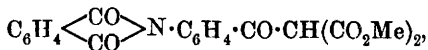
Isomeride III.—This is dimethylisatol, $C_6H_2Me_2 \llcorner \begin{smallmatrix} C(OH) \\ N \end{smallmatrix} \gg CO$. Its methyl ether is converted in the lactim ether by heating with 50% acetic acid.

Isomeride IV.—This substance, in the purest form obtained, crystallises in red needles, m. p. about 315° , sintering above 285° . It appears to contain a different ring system, and it is regenerated when its methyl ether is heated with 50% acetic acid. C. S.

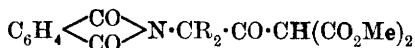
Action of Acylamino-acid Chlorides on Sodiomalonic Esters. V. S. GABRIEL and BRUNO LÖWENBERG (*Ber.*, 1918, 51, 1493—1500).—*o*-Phthaliminobenzoyl chloride,



stout prisms, m. p. 152 — 153° , prepared by heating *o*-phthaliminobenzoic acid with phosphorus pentachloride, reacts with a benzene suspension of methyl sodiomalonate to form the yellow sodium derivative of *methyl o-phthaliminobenzoylmalonate*,

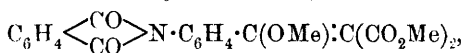


flat prisms, m. p. 159 — 161° . This substance, which is decomposed into methyl iodide, carbon dioxide, phthalic acid, and *o*-aminoacetophenone by boiling hydriodic acid, does not resemble the analogously constituted substances,



previously described by Gabriel (1913—1915) in its behaviour with sodium methoxide, since by treatment with a 4% methyl-alcoholic solution it yields, not the expected 6-ring analogue of the tetramic acids, but first the sodio-derivative, which then decomposes, yielding *methyl o-phthaliminobenzoate*, stout crystals, m. p. 160 — 162° (also prepared from *o*-phthaliminobenzoyl chloride and methyl-alcoholic sodium methoxide), and *methyl 2-o-carboxybenzoylamino-*

benzoate, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$, flat leaflets, m. p. 145—146° (also prepared by heating together methyl anthranilate and phthalic anhydride). A second point of difference is the behaviour of the sodio-derivative on methylation, since by heating with methyl iodide and acetone at 100°, it yields, not a C-methyl derivative, but the O-methyl derivative,



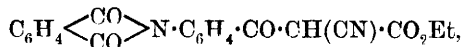
crystals, m. p. 148—149°, which is converted into phthalic and anthranilic acids by boiling hydrochloric or hydrobromic acid, but into methyl iodide, carbon dioxide, and a substance, $\text{C}_{17}\text{H}_{13}\text{O}_5\text{N}$, flat needles or plates, m. p. 248° (decomp.), by hydriodic acid; this substance, which is probably 4-keto-2-o-carboxyphenyl-1:2:3:4-tetrahydroquinoline-3-carboxylic acid, yields carbon dioxide, aniline, and phthalidylacetic acid by heating at 180° with fuming hydrochloric acid.

Ethyl o-phthaliminobenzoylmalonate, $\text{C}_{22}\text{H}_{19}\text{O}_7\text{N}$, prisms, m. p. 101—107°, sintering at 94°, yields *ethyl o-phthaliminobenzoate*, stout prisms, m. p. 108—109°, and *ethyl 2-o-carboxybenzoylamino-benzoate*, needles, m. p. 114—116°, by treatment with sodium methoxide, and its sodio-derivative yields the O-ethyl derivative, $\text{C}_{24}\text{H}_{23}\text{O}_7\text{N}$, m. p. 89—90°, and O-methyl derivative, $\text{C}_{23}\text{H}_{21}\text{O}_7\text{N}$, prisms, m. p. 104—106°, from which the preceding dicarboxylic acid, $\text{C}_{17}\text{H}_{13}\text{O}_5\text{N}$, is obtained by the action of hydriodic acid.

C. S.

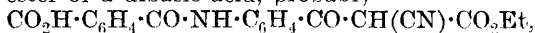
Some Quinoline Derivatives. S. GABRIEL (*Ber.*, 1918, 51, 1500—1515. Compare preceding abstract).—Since *o*-phthaliminobenzoylmalonic esters yield *o*-aminoacetophenone by treatment with acids (*loc. cit.*), *o*-phthaliminobenzoylcianoacetic esters have been prepared in the hope that they would yield *o*-amino- ω -cyanoacetophenone, from which a quinoline derivative could be prepared. These expectations have been fulfilled.

Ethyl sodiocyanoacetate and *o*-phthaliminobenzoyl chloride react in benzene to form the yellow sodio-derivative of *ethyl o-phthaliminobenzoylcianoacetate*,



flat needles, m. p. 178—179°. The latter forms an *ammonium* derivative, yellow prisms, and a *silver* derivative, $\text{C}_{20}\text{H}_{13}\text{O}_5\text{N}_2\text{Ag}$, from which methyl iodide and acetone at 100° produce a *methyl* derivative, crystals, m. p. 173—174°, which is probably the O-ether, $\text{C}_6\text{H}_4\left\langle\begin{smallmatrix}\text{CO} \\ \text{CO}\end{smallmatrix}\right\rangle\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{OMe})\cdot\text{C}(\text{CN})\cdot\text{CO}_2\text{Et}$, since it yields the substance, $\text{C}_9\text{H}_8\text{ON}_2$, (see below) by boiling with hydriodic acid.

When treated with *N*-alkali hydroxide in the cold, and then with hydrochloric acid, ethyl *o*-phthaliminobenzoylcianoacetate yields the ester of a dibasic acid, probably



microscopic prisms or crusts, m. p. 263—265° (decomp.; sintering above 255°), which develops a cherry-red coloration with ferric chloride, and is converted by glacial acetic acid with warming into phthalic acid and 3-cyano-2:4-dihydroxyquinoline, $C_{10}H_6O_2N_2$, colourless needles, m. p. above 300° (decomp.; sintering at about 270°); the last substance is converted into 2:4-dihydroxyquinoline by boiling hydriodic acid, and into 2:4-dichloro-3-cyanoquinoline, colourless needles, m. p. 168—169°, by boiling with phosphoryl chloride and phosphorus pentachloride for one and a-half hours. If the boiling proceeds for only half an hour, the product is 4(or 2)-chloro-3-cyano-2(or 4)-hydroxyquinoline, flat needles, not molten at 280°. The dichlorocyanquinoline is converted into kynurenic acid by boiling hydriodic acid (b. p. 127°) and red phosphorus.

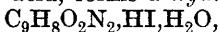
By boiling with hydrobromic or, better, hydriodic acid, ethyl *o*-phthaliminobenzoylcyanacetate is converted into phthalic acid and a substance, $C_9H_8ON_2$, long needles with $1H_2O$ from water or anhydrous crystals from alcohol, m. p. about 303—304°, sintering at about 285°, which forms a *hydrobromide*, $C_9H_8ON_2 \cdot HBr$, slender needles, *platinichloride*, and *aurichloride*, and is proved to be 2-amino-4-hydroxyquinoline, the intermediately formed *o*-amino-*o*-cyanoacetophenone not being isolated; a by-product of the reaction is 2:4-dihydroxyquinoline.

By treatment with nitric (D 1.30) and glacial acetic acids on the water-bath, 2:4-dihydroxyquinoline is converted into 3-nitro-2:4-dihydroxyquinoline, sulphur-yellow prisms, decomp. about 225°, which possesses pronounced acid properties and yields 2:4-dichloro-3-nitroquinoline, needles, m. p. 102°, by heating with phosphoryl chloride; the last substance is reduced to 3-aminoquinoline by tin and hydrochloric acid.

o-Nitrobenzoyl chloride reacts with ethyl sodiocyanacetate in the presence of ether to form, after treatment of the initial product with hydrochloric acid, ethyl *o*-nitrobenzoylcyanacetate, $NO_2 \cdot C_6H_4 \cdot CO \cdot CH(CN) \cdot CO_2Et$, needles, m. p. 91°, which is reduced and hydrolysed by boiling hydriodic acid and red phosphorus, yielding ethyl iodide, carbon dioxide, and 2-amino-4-hydroxyquinoline. The aminohydroxyquinoline is converted by very dilute hydrochloric acid and alkali nitrite (1 mol.) into the *iminoquinisatoxime*, $C_6H_4 \begin{smallmatrix} NH \cdot C \cdot NH \\ | \\ CO \cdot C \cdot N \cdot OH \end{smallmatrix}$ or $C_6H_4 \begin{smallmatrix} N = C \cdot NH_2 \\ | \\ CO \cdot C \cdot N \cdot OH \end{smallmatrix}$, which forms a *potassium salt*, $C_6H_4O_2N_3K$, garnet-red needles, and a *hydrochloride*, $C_9H_7O_2N_3 \cdot HCl$, orange-yellow needles, yields 3-nitro-2:4-dihydroxyquinoline by warming with nitric acid (D 1.34), and is reduced by tin and 20% hydrochloric acid to the *hydrochloride*, colourless crystals containing $1H_2O$, of a *base*, $C_9H_8O_2N_2$, needles containing $1H_2O$, not molten at 300°, which is probably 2-amino-3:4-dihydroxyquinoline. By trituration with hydriodic acid (b. p. 127°), the iminoquinisatoxime is converted into 2:3-diamino-4-hydroxyquinoline, flat needles (*hydrochloride*, $C_9H_9ON_3 \cdot 2HCl$, needles).

The reduction of *quinisatoxime* by hydriodic acid or by tin and

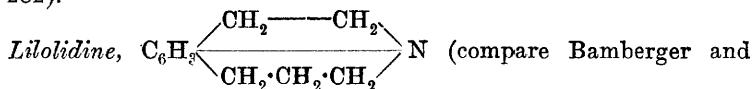
20% hydrochloric acid yields the *hydrochloride*, $C_9H_8O_2N_2 \cdot HCl \cdot H_2O$, colourless needles, not molten at 285° , of 3-*amino*-2:4-*dihydroxyquinoline*, microscopic needles, not molten at 280° . The base, which is also obtained by reducing 3-nitro-2:4-dihydroxyquinoline by tin and hydrochloric acid, forms a *hydriodide*,



colourless needles, and an *acetyl* derivative, darkening above 200° , but not molten at 285° .

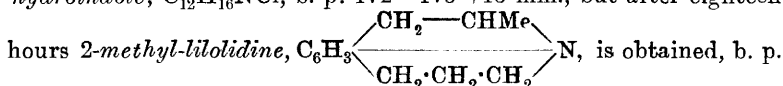
C. S.

Bases of the Julolidine Type. J. VON BRAUN, KARL HEIDER, and WANDA WYCZATKOWSKA (*Ber.*, 1918, **51**, 1215—1227).—Such bases are of interest in connexion with the phenomena of steric hindrance in tertiary bases and the fission of hydrogenised indole and quinoline derivatives by sodium amalgam (von Braun, A., 1917, i, 282).



Sternitzki, A., 1893, i, 520), b. p. $156^\circ/15$ mm., cannot be prepared from tetrahydroquinoline and ethylene dibromide, but is produced by gently boiling a mixture of dihydroindole (1 part) and γ -chloropropyl bromide (6 parts) for eighteen hours. It forms a *picrate*, m. p. 138° , and a *methiodide*, and resembles dimethylaniline in its behaviour towards formaldehyde, yielding a viscous diphenylmethane derivative, $CH_2(C_{11}H_{12}N)_2$, and towards benzaldehyde in the presence of zinc chloride, yielding ultimately an intensely green substance. The *methochloride* exhibits remarkable stability towards 5% sodium amalgam, the rings being unbroken and lilolidine being regenerated. This stability is in marked contrast to those of the methochlorides of tetrahydroquinoline and dihydroindole, in which the rings are ruptured to the extent of 60% and 25% respectively.

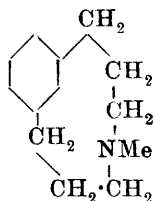
2-Methyldihydroindole and γ -chloropropyl bromide, boiled together for four to five hours, yield 2-methyl-1- γ -chloropropyl-dihydroindole, $C_{12}H_{16}NCl$, b. p. $172\text{---}175^\circ/15$ mm., but after eighteen



$165\text{---}167^\circ/15$ mm., which forms a *picrate*, m. p. 140° , and a *methiodide*, m. p. 202° , resembles lilolidine in its behaviour towards formaldehyde and benzaldehyde, and the *methochloride* of which is mainly unruptured by sodium amalgam, only about 10% of it being converted into a *base*, $C_{13}H_{19}N$, colourless oil, b. p. $151^\circ/15$ mm. (*picrate*, yellow needles, m. p. 121° ; *platinichloride*, m. p. $177\text{---}178^\circ$). This base, which yields a *m*-diamine by nitration and subsequent reduction, must be 1:2-dimethyl-7-n-propyldihydroindole, because it is not identical with the only other substance possible, namely, 8-n-propylkairolone. The last-mentioned substance was synthesised as follows: *o*-Propylaniline, obtained from tetrahydroquinoline through *o*- γ -chloropropylbenzanilide, is converted by

the Skraup method into 8-propylquinoline, b. p. 142°/15 mm. (*platinichloride*, m. p. 196°; *picrate*, yellowish-red needles, m. p. 142°), the *methiodide*, m. p. 136°, of which is reduced by tin and hydrochloric acid to 8-n-propylkairolin (*picrate*, m. p. 108—109°; *platinichloride*, m. p. 164°).

Julolidine, prepared by Pinkus's method (A., 1892, 1491. For large quantities of materials the time of heating must be prolonged to eight hours to prevent the formation of halogenated impurities), resembles the lilolidines in its behaviour towards benzaldehyde and formaldehyde (the oily diphenylmethane derivative yields a *dimethiodide*, $C_{27}H_{36}N_2I_2$, colourless crystals, m. p. 228°), and forms a methiodide much more readily than does 8-methylkairolin or dimethyl-*o*-toluidine. The *methochloride* by reduction with 5% sodium amalgam yields 63% of julolidine and 37% of a *base*, $C_{18}H_{19}N$, b. p. 144—148°/23 mm. (*picrate*, yellow needles, m. p. 189°, decomposition beginning above 180°; *platinichloride*, m. p. 191°; *methiodide*, colourless crystals, m. p. 200°), which is not the expected 8-n-propylkairolin, but appears to have the annexed formula. It is remarkable in that it contains a 10-ring, and is a meta-bicyclic compound. It is a saturated substance, yields isophthalic acid by oxidation with alkaline permanganate, does not condense with benzaldehyde to give ultimately a green colouring matter, does not yield a meta-diamine by nitration and subsequent reduction, and its methiodide, after treatment with silver oxide and distillation, yields a *base*, $C_{14}H_{21}N$, b. p. 117—118°/3 mm., which does not form crystalline salts, is unsaturated and is regarded as γ -3-allylphenyl-n-propyldimethylamine, $CH_3 \cdot CH \cdot CH_2 \cdot C_6H_4 \cdot [CH_2]_3 \cdot NMe_2$.



C. S.

Proteinogenous Amines. I. Synthesis of β -Iminazolyethylamine [Histamine]. KARL K. KOESSLER and MILTON TH. HANKE (*J. Amer. Chem. Soc.*, 1918, **40**, 1716—1726).—The method followed is based on that of Pyman (T., 1911, **99**, 668), but several additions and improvements have been effected. Full descriptions are given of the preparation of acetonedicarboxylic acid, dioximinoacetone, diaminoacetone stannichloride, diaminoacetone hydrochloride, 2-thiol-4(or 5)-aminomethylglyoxaline hydrochloride, 4(or 5)-hydroxymethylglyoxaline picrate, 4(or 5)-hydroxymethylglyoxaline hydrochloride, and of iminazolyethylamine dichloride (histamine dichloride); the separation of methylglyoxaline and of glyoxalineacetic acid is also described. One hundred and sixty-five grams of histamine dichloride are obtained from 4530 grams of citric acid.

H. W.

Phenomena of Luminescence in Pyrazoline Derivatives. FRITZ STRAUS [with CARL MUFFAT and W. HEITZ] (*Ber.*, 1918, **51**, 1457—1477).—In consequence of the striking ease with which pyrazolines are obtained directly by the action of phenylhydrazine

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on phenyl styryl ketone, distyryl ketone, and ethyl γ -keto- $\Delta^{\alpha\beta}$ -pentadiene- $\alpha\epsilon$ -dicarboxylate, the intermediary phenylhydrazones not being isolable, and of the phenomena of luminescence exhibited by these substances, the reaction has been extended to include a series of substituted ketones and substituted hydrazines. It is found that pyrazolines are formed except (1) when *p*-nitrophenylhydrazine is used, (2) when an *o*-methoxy-group is present in the phenyl group of the ketone, and (3) when the phenylhydrazine and a phenyl group of the ketone both contain a halogen substituent; in these three cases the phenylhydrazones or substituted phenylhydrazones are stable, and require special treatment for their conversion into pyrazolines.

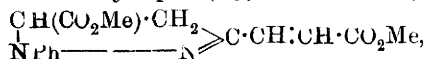
The following substances are described. The method of von Auwers and Voss (A., 1910, i, 70), reduction by sodium amalgam with the formation of aniline, is used to distinguish the phenylhydrazones from the pyrazolines.

1- α -Naphthyl-5-phenyl-3-styrylpyrazoline, prepared from distyryl ketone and α -naphthylhydrazine in boiling alcohol, forms yellow needles with green fluorescence, m. p. 164°; the β -naphthyl isomeride, m. p. 195°, has a similar appearance. 5-Phenyl-1-*p*-bromophenyl-3-styrylpyrazoline, prepared in glacial acetic acid solution at the ordinary temperature, forms yellow needles with green fluorescence, m. p. 177°. Distyryl ketone *p*-nitrophenylhydrazone, yellowish-red leaflets, m. p. 173°, yields *p*-phenylenediamine by reduction with sodium amalgam, and is converted into 5-phenyl-1-*p*-nitrophenyl-3-styrylpyrazoline, yellowish-red crystals with intense green fluorescence, m. p. 204—205°, by boiling glacial acetic acid. Di-*o*-methoxystyryl ketone phenylhydrazone, brownish-yellow crystals, m. p. 142°, is converted into 1-phenyl-5-*o*-methoxyphenyl-3-*o*-methoxystyrylpyrazoline, pale yellow crystals with greenish-blue fluorescence, m. p. 153—154·5°, in a similar manner. 1-Phenyl-5-*p*-methoxyphenyl-3-*p*-methoxystyrylpyrazoline, prepared in boiling benzene, or, more simply, hot glacial acetic acid solution, forms pale yellow leaflets, m. p. 159°, which are so intensely fluorescent that they appear almost green. 1-Phenyl-5-*p*-dimethylaminophenyl-3-*p*-dimethylaminostyrylpyrazoline forms yellow needles, m. p. 192°, which exhibit an extraordinarily intense green fluorescence.

Di-*o*-chlorostyryl ketone, yellow needles, m. p. 125°, prepared from *o*-chlorobenzaldehyde and acetone in 5% boiling alcoholic sodium methoxide solution, reacts with *p*-bromophenylhydrazine by prolonged keeping in glacial acetic acid in the cold to form the *p*-bromophenylhydrazone, C₂₃H₁₇N₂Cl₂Br, dark yellow crystals, m. p. 145°, but yields by treatment with phenylhydrazine in boiling alcohol containing a little acetic acid 1-phenyl-5-*o*-chlorophenyl-3-*o*-chlorostyrylpyrazoline, yellow needles, m. p. 145°, forming a green, fluorescent solution in alcohol. 1-Phenyl-5-*p*-chlorophenyl-3-*p*-chlorostyrylpyrazoline, m. p. 212°, forms yellow needles with intense green fluorescence; its solution in concentrated sulphuric acid is so slightly coloured by ferric chloride that some doubt would exist as to the substance being a pyrazoline were it not that aniline is not

produced by its reduction by sodium amalgam. *Di-p-chlorostyryl ketone p-bromophenylhydrazone*, yellow needles, m. p. 183°, which become brown in air, yields *p*-bromoaniline by reduction with sodium amalgam, and is converted into 5-*p*-chlorophenyl-1-*p*-bromophenyl-3-*p*-chlorostyrylpyrazoline, yellow needles with intense green fluorescence, m. p. 173—174°, by boiling glacial acetic acid.

Methyl 5-carbomethoxy-1-phenylpyrazoline-3-acrylate,



m. p. 153°, yellow leaflets with a striking green fluorescence, is prepared from phenylhydrazine and methyl γ -keto- Δ^{α} -pentadiene- α -dicarboxylate (Straus, A., 1904, i, 851) in boiling benzene. The *ethyl ester*, $\text{C}_{17}\text{H}_{20}\text{O}_4\text{N}_2$, yellow, fluorescent leaflets, m. p. 92.5°, yields the *acid*, $\text{C}_{13}\text{H}_{12}\text{O}_4\text{N}_2$, yellow needles, m. p. 204° (decomp.), by hydrolysis with aqueous-alcoholic sodium hydroxide on the water-bath. The preceding methyl ketopentadienedicarboxylate forms a *phenylmethylhydrazone*, $\text{C}_{16}\text{H}_{18}\text{O}_4\text{N}_2$, dark red crystals, m. p. 105°, and the ethyl ester forms a *p-bromophenylhydrazone*, $\text{C}_{17}\text{H}_{19}\text{O}_4\text{N}_2\text{Br}$, reddish-yellow needles, m. p. 134°.

When boiled with glacial acetic acid, the phenylhydrazones of phenyl cinnamylidenemethyl ketone and of dicinnamylidenemethyl ketone are converted respectively into substances, $\text{C}_{23}\text{H}_{20}\text{N}_2$, colourless crystals with faint blue fluorescence, m. p. 123—124°, and $\text{C}_{27}\text{H}_{24}\text{N}_2$, orange-yellow needles, m. p. 142°, which are not pyrazolines because they cannot be oxidised to the pyrazolinecarboxylic acids.

Straus and Ackermann's *p*-chlorophenyl *p*-chlorostyryl ketone phenylhydrazone (A., 1909, i, 489) is really 1-phenyl-3:5-di-*p*-chlorophenylpyrazoline, and Minnuni's distyryl ketone phenylhydrazone (A., 1900, i, 237) is 1:5-diphenyl-3-styrylpyrazoline.

All the pyrazolines examined exhibited the most intense fluorescence when exposed to Röntgen rays. An apparatus is described by which several substances can be simultaneously but separately exposed to the rays with or without passage through zinc foil, and the intensities of the fluorescence compared with that of barium platinocyanide. The fluorescence is still visible after the rays have passed through zinc foil 0.6 mm. in thickness. A new noteworthy fact is that the fluorescence is observed, not only with the crystalline substances, but also with their solutions, the intensity being greatly influenced by the nature of the solvent. In the case of a 1% solution of the ester of 5-carboxy-1-phenylpyrazoline-3-acrylic acid, the solutions in alcohol and glacial acetic acid were only feebly fluorescent, and the fluorescence was destroyed by interposing zinc foil 0.2 mm. thick, but the solutions in carbon disulphide, benzene, and chloroform were intensely fluorescent, and a thickness of 1 mm. of zinc foil was necessary to destroy it.

There is a noteworthy difference between the fluorescence of the 1:3:5-trisubstituted pyrazolines excited by Röntgen rays and that produced by diffuse daylight. The excitation of Röntgen rays occurs

within narrow limits, and is connected with the presence of an unsaturated group (phenyl or carbonyl) in positions 3 and 5; if these positions are occupied by hydrogen or by an aliphatic group the pyrazoline fluoresces in diffuse daylight, but is unaffected by Röntgen rays. The effects on the intensity of the fluorescence of substituents in phenyl groups in positions 1, 3, and 5 are discussed. The phenylhydrazones of unsaturated ketones are intensely coloured, but do not exhibit a trace of fluorescence. C. S.

Preparation of Mercurous Amino-compounds. SCHWEIZ. SERUM- & IMPFINSTITUT (D.R.-P., 307893; from *Chem. Zentr.*, 1918, ii, 693).—The compounds are prepared by the action of one or more molecules of a mercurous salt on 1-phenyl-2:3-dimethyl-5-pyrazolone-4-sulphonamide. The *substance* obtained with mercurous sulphate (1 mol.) is a greyish-white, crystalline mass, which darkens and swells when heated; it is specifically lighter than mercurous sulphate, and contains 40% of mercury. On treatment with alkali it yields a precipitate of mercury and a soluble mercuric amino-compound, which is precipitated by hydrogen sulphide after acidification with hydrochloric acid. With two molecules of mercurous sulphate a complex *substance* is formed. The compounds are stable in substance and also when emulsified with fats. They have marked bactericidal and spirilloidal properties. H. W.

Salts of Helianthin. CHARLES R. STARK and WILLIAM M. DEHN (*J. Amer. Chem. Soc.*, 1918, **40**, 1573—1580).—Recent studies with methyl-orange (Dehn, A., 1917, i, 594) have led to the conclusion that colour changes in solution are largely or wholly independent of ionic concentrations. It has been suggested that the coloured solute forms additive compounds with acids, bases, or indifferent solvents. In the present communication it is shown that helianthin forms salts with great ease, all of which can be interpreted as additive compounds.

The helianthin salts of bases were prepared (1) from aqueous solutions of helianthin and the free base, (2) by double decomposition from methyl-orange and the salt of the base, (3) by adding helianthin to the pure liquid base, and (4) by treating helianthin with an excess of the base dissolved in absolute ether. In the preparation of helianthin salts with acids, the presence of water must be avoided; the salt is conveniently obtained by dissolving helianthin in excess of the warm acidic solvent and subsequently adding ether.

Salts of helianthin prepared in aqueous solution with inorganic bases always contain two molecules of water to each helianthin residue. The salts made with ammonia or volatile organic bases give free helianthin when heated; those containing the coloured ions Cr'' , Cu'' , Co'' , Ni'' , Fe'' or Fe''' give no evidence of the presence of these ions if they are judged only by the colour; when dehydrated, all helianthin salts containing the bivalent and trivalent metals, but not the univalent metals, tend to form the colour of helianthin itself. The salts of organic bases are always additive compounds of the type $\text{C}_{14}\text{H}_{14}\text{N}_3\text{SO}_3\text{H}$ base. The salts with the

following metals or bases are described: *Aluminium*, golden, rhombic plates; ammonium, m. p. 225°, large golden-red, rhombic plates; *barium*, golden-brown, rhombic plates; *cadmium*, golden-red rhombic plates; *calcium*, orange needles and rhombic plates; *chromium*, golden-brown, rhombic plates; *cobalt*, golden-red, hexagonal and rhombic plates; *copper*, pale golden-brown, rhombic plates; *ferrous*, m. p. 209°, golden-brown, rhombic plates; *ferric*, reddish-golden, irregular and rhombic plates; *lead*, brown masses and irregular plates; *magnesium*, reddish-gold, hexagonal and rhombic plates; *manganese*, pale reddish-gold, irregular and rhombic plates; *silver*, dull brownish-red needles; *sodium*, m. p. 224°; *nickel*, light golden-red, hexagonal and rhombic plates; *potassium*, orange, hexagonal plates, m. p. 300°; *strontium*, brilliant orange, rhombic plates and needles; *uranium*, orange-red, rhombic plates; *zinc*, golden-brown, rhombic plates, m. p. 241°; *aniline*, golden-orange, prismatic flakes and needles, m. p. 211°; *benzidine*, golden-brown, irregular and rectangular plates and needles, m. p. 198° after changing at 194°; *brucine*, orange, prismatic needles, m. p. 224°; *cinchonidine*, light yellow, prismatic needles and irregular plates, m. p. 155°, after changing at 146°; *dimethylaniline*, needles and hexagonal plates; *methylaniline*, thin, golden-brown prisms and rhombic and hexagonal plates, m. p. 167°; *morphine*, bright orange, irregular plates and sheaves and wart-like masses of prisms, m. p. 219°; *α -naphthylamine*, dull brown needles, m. p. 211°; *β -naphthylamine*, brownish-yellow, thin, irregular plates, m. p. 209°; *phenylhydrazine*, orange needles and rectangular plates, m. p. 165°; *α -picoline*, dark brownish-red, rectangular and octagonal plates, m. p. 180°, after changing at 157°; *nineridine*, bright orange, octagonal and irregular plates, m. p. 223°; *quinine*, orange, amorphous mass, m. p. 158°; *quinoline*, orange-red prisms and octagonal plates, m. p. 194°; *strchnine*, golden-orange prisms and rectangular and irregular plates, m. p. 254°; *o-toluidine*, orange-red, prismatic needles, m. p. 203°; *m-toluidine*, golden-yellow needles and irregular plates, m. p. 202°.

Helianthin phenolate forms dark purple prisms, m. p. 200°.

The solubilities of the salts in water and their behaviour when heated are recorded in a series of tables, for which the original must be consulted.

H. W.

Synthesis of some New Substantive Dyes derived from Benzidine-Sulphone. HUGH RYAN, JOSEPH ALGAR, and PHILIP O'CONNELL (*Proc. Roy. Irish Acad.*, 1918, **34**, (B), 85—96).—A series of dyes of the benzidine type has been prepared by coupling hydroxy- and amino-compounds with the tetrazo-derivative of benzidine-sulphone-disulphonic acid. The dyes have been isolated in the form of pure sodium salts; they act as direct dyes towards cotton and the colours are unaffected by washing. *Products* have been obtained with the following substances, the shade obtained on cotton being placed within brackets: naphthionic acid, dull blue, amorphous powder (purple); β -naphthylamine, red, amorphous

powder (violet-red); α -naphthylamine, dark red powder (navy blue); salicylic acid, reddish-brown powder (orange); "R" acid, reddish-blue powder (violet-red); "S" acid, red, amorphous powder (pink); "H" acid, dark blue powder (light blue); β -naphthol-6-monosulphonic acid, dark blue, amorphous powder (light purple); catechol, dark blue powder (light brown); resorcinol, dark blue powder (maroon); quinol, brown powder (buff); pyrogallol, chocolate-brown powder (buff); gallic acid, dark brown powder (light brown); sulph-anilic acid, orange-red, amorphous powder (canary-yellow); dimethylaniline, dark blue powder (deep purple). H. W.

Influence of Substituents on Reactions. II. Rate of Reduction of Polymethylphenylhydrazines. HARTWIG FRANZEN, ARVID ONSAGER, and GUNNAR FAERDEN (*J. pr. Chem.*, 1918, [ii], **97**, 336—352. Compare A., 1918, i, 456).—Continuing the previous investigation, the authors have examined the rate of reduction by stannous chloride and hydrochloric acid of phenylhydrazines containing several nuclear methyl substituents. In the case of the dimethylphenylhydrazines the series, arranged in order of decreasing ease of fission, is precisely that which would be predicted from the previous results, the values of the constant K' being: 2:6-dimethylphenylhydrazine, 4.19; 2:4-, 2.49; 2:3-, 0.130; 2:5-, 0.107; 3:4-, 0.102. The 3:5-compound has been only provisionally examined, and its rate of reduction appears to be less than that of the 3:4-compound.

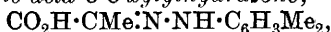
The only trimethylphenylhydrazines that have been examined are the 2:4:6- and 2:4:5-compounds. The entrance of yet another methyl group still further increases the ease of fission by stannous chloride and hydrochloric acid. These two compounds are reduced so rapidly at 100° that measurements cannot be made. At 80° the k' value of the former is 3.99 and of the latter 1.05. These values will be about six times as great at 100°, so that at this temperature 2:4:6-trimethylphenylhydrazine is reduced about six times more rapidly than 2:6-dimethylphenylhydrazine and about 1200 times more rapidly than phenylhydrazine itself.

The striking parallelism traced between the rate of reduction of substituted phenylhydrazines and the rate of dehalogenation of correspondingly substituted halogenobenzenes by hydriodic acid (*loc. cit.*) is still more evident in the case of the dimethylphenylhydrazines and the iododimethylbenzenes. After boiling with hydriodic acid for five hours the amounts of xylene obtained are: from 2-iodo-1:3-dimethylbenzene, 80%; from 4:1:3-, 60%; from 3:1:2-, trace; from 2:1:4-, trace; from 1:3:5-, 0%. 2-Iodo-1:3:5-trimethylbenzene yields 50% of mesitylene after boiling for five hours and 90% after being heated at 140° for five hours, the corresponding values for 5-iodo-1:2:4-trimethylbenzene being 0% and 85% of ψ -cumene respectively.

The polymethylphenylhydrazines required in the investigation were prepared by reducing the diazonium chlorides with stannous chloride and hydrochloric acid. In several cases the yields were

very bad, as low as 7.5%, in consequence of the reaction $\text{ArN}_2\text{Cl} + 2\text{H} = \text{ArH} + \text{N}_2 + \text{HCl}$ becoming the main reaction. A relation was found to exist between the rate of reduction of the polymethylphenylhydrazines and the tendency of the corresponding diazonium chlorides to yield the phenylhydrazine or the hydrocarbon and nitrogen on reduction; the more easily the phenylhydrazine is reduced the greater is the tendency of the corresponding diazonium chloride to yield the hydrocarbon and nitrogen on reduction.

3-*o*-Xylylhydrazine, colourless needles, m. p. 108°, forms a *hydrochloride*, colourless leaflets, m. p. 208°, *benzylidene* derivative, $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{NH}\cdot\text{N}:\text{CHPh}$, yellow crystals, m. p. 68°, *p*-anisylidene derivative, dark yellow, crystalline powder, m. p. 98°, and *dibenzoyl* derivative, $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{NBz}\cdot\text{NHBz}$, colourless, crystalline powder, m. p. 198°. *Pyruvic acid* 3-*o*-xylylhydrazone,



forms yellow leaflets, m. p. 166°.

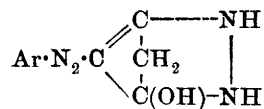
2:4:6-Trimethylphenylhydrazine hydrochloride forms faintly yellow leaflets. C. S.

Synthesis of New Chloroarylhydrazones of Oxalomono-ester and -mono-amide Acid Chlorides and of the Corresponding Nitriles. CARL BÜLOW and RICHARD ENGLER (*Ber.*, 1918, **51**, 1246—1270).—In consequence of its decomposition by heat into carbon monoxide and ethyl malonate, ethyl oxalacetate

is represented by the "aliphatic cyclic" structure, $\text{CO} < \begin{array}{c} \text{CH}-\text{CO}_2\text{Et} \\ | \\ \text{C}(\text{OH})\cdot\text{OEt} \end{array}$

(compare Bülow and Huss, A., 1918, i, 314); citric acid, ethyl acetonedicarboxylate, ethyl formylacetate, ethyl acetoacetate, and acetylacetone are represented by similar 3-ring and 4-ring structures containing the group $\cdot\text{CH}:\text{C}(\text{OH})\cdot$ similar to that in β -naphthol, and therefore reacting with diazonium salts. Ethyl *o*-tolueneazoacetoacetate, for example, is represented by the formula $\text{C}(\text{OH})\cdot\text{C}\cdot\text{N}_2\cdot\text{C}_7\text{H}_7$, $\text{CH}_2-\text{C}(\text{OH})\cdot\text{OEt}$. This substance, previously prepared by Bülow

and Schaub (A., 1908, i, 704), has m. p. 52° (Bülow and Schaub give 67°), yields the corresponding *potassium* salt, yellow needles, by hydrolysis with boiling 1% potassium hydroxide, and by treatment with concentrated nitric acid and subsequently with water is converted into nitrated *o*-toluenediazonium nitrate and ethyl acetoacetate. When treated with concentrated nitric acid in cold glacial acetic acid solution, however, it yields *ethyl nitro-o-tolueneazoacetoacetate*, needles, m. p. 135—136°, since the product and hydrazine hydrate in hot glacial acetic acid yield 4-*nitro-o-tolueneazo-3-methylpyrazolone*, yellowish-orange needles, m. p. 223—224° (decomp.). To azopyrazolones the authors



give the formula (annexed). By chlorination in cold alcoholic solution and repetition of the treatment on the initial product in warm alcohol, ethyl *o*-tolueneazoacetoacetate yields *ethyl α -chloroglyoxylate*

5-chloro-*o*-tolylhydrazone, $C_6H_3MeCl \cdot NH \cdot N : CCl \cdot CO_2Et$, colourless needles, m. p. 110° , which yields 5-chloro-*o*-toluidine by reduction with hydrochloric acid and zinc dust, and is converted by potassium cyanide in aqueous-alcoholic solution into ethyl α -cyanoglyoxylate 5-chloro-*o*-tolylhydrazone, $C_6H_3MeCl \cdot NH \cdot N : C(CN) \cdot CO_2Et$, golden-yellow needles, m. p. 163.5° , identical with the substance prepared by condensing diazotised 5-chloro-*o*-toluidine and ethyl cyanoacetate. The product obtained by the latter method is a labile form, which changes at its m. p., 106.5° , into the stable form, m. p. 163.5° . Ethyl α -chloroglyoxylate 5-chloro-*o*-tolylhydrazone resembles ethyl *o*-tolueneazoacetate in its behaviour with concentrated nitric acid and exhibits halochromy when dissolved in concentrated sulphuric acid, the solution developing an intense yellow colour, which changes very rapidly to a dirty brownish-green, and regenerating the original substance on the addition of water. Ethyl α -cyanoglyoxylate 5-chloro-*o*-tolylhydrazone, by treatment with concentrated nitric acid at about 40 – 50° and subsequently with water, yields a nitrated product, m. p. 121 – 122° , together with a comparatively large amount of a diazonium nitrate.

By treatment with 96% alcohol and aqueous ammonia, ethyl *o*-tolueneazoacetate yields, in addition to a small amount of the ammonium salt, m. p. 202° (decomp.), *o*-tolueneazoacetamide, golden-yellow needles, m. p. 142° , which yields nitro-*o*-tolueneazoacetamide, m. p. 243 – 244° , and only a trace of a diazonium salt by treatment with concentrated nitric acid at about 45° . The preceding ammonium salt yields *o*-tolueneazoacetic acid, greenish-yellow needles, m. p. 137 – 138° , by treatment with glacial acetic acid.

Ethyl *p*-tolueneazoacetate is very readily converted into the corresponding potassium salt by boiling 1–2% potassium hydroxide and resembles the ortho-isomeride in its behaviour towards concentrated nitric acid, yielding partly a diazonium salt by fission and partly ethyl nitro-*p*-tolueneazoacetate, m. p. 143 – 144° , which is converted into 4-nitro-*p*-tolueneazo-3-methylpyrazolone, m. p. 234° , by hydrazine hydrate in glacial acetic acid solution.

Ethyl α -chloroglyoxylate 3-chloro-*p*-tolylhydrazone, m. p. 100° , is prepared like the preceding *o*-tolyl isomeride, but when chlorinated in carbon tetrachloride at 0° ethyl *p*-tolueneazoacetate yields ethyl α -chloroglyoxylate *p*-tolylhydrazone, colourless needles, m. p. 101 – 101.5° . Both these hydrazones yield diazonium salts by treatment with nitric acid. The former reacts with potassium cyanide to form ethyl α -cyanoglyoxylate 3-chloro-*p*-tolylhydrazone, golden-yellow needles, m. p. 160° , which undergoes both nitration and fission by treatment with nitric acid, and in cold, alcoholic suspension reacts with chlorine in a unique manner, yielding 3-chloro-*p*-toluenediazonium chloride, ammonium chloride, and the decomposition products of ethyl hydrogen dichloromalonate. Ethyl α -chloroglyoxylate 3-chloro-*p*-tolylhydrazone yields 3-chloro-*p*-toluidine by reduction with hydrochloric acid and zinc dust. Ethyl α -cyanoglyoxylate 3-chloro-*p*-tolylhydrazone has also been prepared

by condensing diazotised 3-chloro-*p*-toluidine with ethyl cyanoacetate.

p-Tolueneazoacetoacetamide, prepared by treating an alcoholic solution of ethyl *p*-tolueneazoacetoacetate with a large excess of concentrated aqueous ammonia, forms pale green leaflets, m. p. 173°, yields nitro-*p*-tolueneazoacetoacetamide, m. p. 211—212°, and a little diazonium salt by treatment with concentrated nitric acid, and yields by chlorination in boiling alcoholic solution α -chloroglyoxylamide 3-chloro-*p*-tolylhydrazone, $C_6H_3MeCl \cdot NH \cdot N : CCl \cdot CO \cdot NH_2$, colourless needles; the constitution $C_6H_3MeCl \cdot NH \begin{smallmatrix} \nearrow NH=CCl \\ \searrow NH-CO \end{smallmatrix}$ is suggested to account for the absence of colour. C. S.

Preparation of Bromolecithalbumin and Bromolecithin. PETER BERGELL (D.R.-P., 307490; from *Chem. Zentr.*, 1918, ii, 494—495).—Lecithalbumin is treated with bromine in anhydrous, indifferent organic solvents, and, when required, the bromolecithalbumin is decomposed into bromolecithin and albumin according to the method of converting lecithalbumin into lecithin. *Bromolecithalbumin* is a pale yellow, almost odourless powder with a faintly acid taste and reaction; it contains about 16.6% of bromine. It is transformed by methyl or ethyl alcohol, slowly in the cold more rapidly on warming, into albumin and *bromolecithin* containing up to 25% of bromine. H. W.

The Relationship between Diastase, Peroxydase, and Catalase. H. MAGGI (*Helv. Chim. Acta*, 1918, 1, 433—451).—The simultaneous presence of peroxydase and catalase activity in many ferments has been attributed by Woker (A., 1917, i, 447) to the presence of an aldehydic group which unites with hydrogen peroxide to yield a secondary peroxide, $OH \cdot CHR \cdot O \cdot OH$, which has more powerful oxidising properties than hydrogen peroxide itself and also reacts with an excess of the latter to yield oxygen. The author has examined the question of the possibility of the aldehyde group being able to exert diastatic action, in addition to peroxydising and catalytic action, and suggests that the mechanism would consist in the alternate addition (to form a hydrate) and elimination of water.

The action of mixtures of starch and formaldehyde has been investigated by the capillarity method; the presence of dextrans is detected by means of iodine and of sugars by Fehling's solution. The results show that the behaviour of formaldehyde towards starch closely resembles that of diastase. One considerable difference, the recurrence of the blue coloration with lapse of time in the case of mixtures of formaldehyde and starch, has been further investigated. The phenomenon appears to be due to the formation of unstable iodine derivatives of formaldehyde or of the achroodextrins which gradually eliminate iodine. The following conditions are necessary: (i) unchanged starch, and (ii) a substance capable of liberating iodine, must be present; if these conditions are fulfilled, any

elimination of achroodextrins by combination, fission, or by any other method can restore the blue colour to the solution. H. W.

Nitro- and Amino-arylsarsinic Acids. WALTER A. JACOBS, MICHAEL HEIDELBERGER and IDA P. ROLF (*J. Amer. Chem. Soc.*, 1918, **40**, 1580—1590).—The preparation of a number of nitro- and amino-arylsarsinic acids is described; the nitro-compounds are generally obtained by Bart's method (D.R.-P., 250264), in which a diazo- or isodiazo-group is replaced by the arsinic acid residue. This procedure is particularly serviceable with *o*- and *p*-nitroamines; with *m*-nitroamines, on the other hand, the yields are poor, though better with *m*-nitrotoluidines than with *m*-nitroaniline. Reduction of the nitro- to the amino-group without disturbance of the arsinic acid residue is conveniently effected with cold, alkaline ferrous hydroxide solution (compare Benda, A., 1912, i, 63). The following compounds have been prepared by these methods:—*o*-nitrophenylarsinic acid, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{AsO}(\text{OH})_2$, m. p. 235—240° (decomp.) [compare Bart, *loc. cit.*]; *o*-aminophenylarsinic acid (compare Benda, *loc. cit.*), needles, m. p. 153°; *m*-aminophenylarsinic acid (compare Bertheim, A., 1908, i, 590; Bertheim and Benda, A., 1912, i, 62), colourless, rhombic prisms, m. p. 213—215° (decomp.); *p*-nitrophenylarsinic acid (compare Bart, *loc. cit.*), pale yellow aggregates of minute leaflets, which do not melt below 275°; *p*-aminophenylarsinic acid; 2-nitro-*p*-tolylarsinic acid, faintly yellow, minute rods, m. p. 255—260° (decomp.); 2-amino-*p*-tolylarsinic acid, colourless needles, m. p. 180°, after softening and darkening; 6-nitro-*o*-tolylarsinic acid, pale yellow needles decomposing at 228—230°; 6-amino-*o*-tolylarsinic acid, rosettes or plates decomposing at 175—180°; 5-nitro-*p*-tolylarsinic acid (compare Michaelis, A., 1902, i, 411), cream-coloured needles which do not melt below 285°; 5-amino-*p*-tolylarsinic acid, microscopic needles, m. p. 172—175°; 5-nitro-*o*-tolylarsinic acid (compare Karrer, A., 1915, i, 333), m. p. 261—263° (decomp.), after melting or changing in appearance at about 225° according to the rate of heating; 5-amino-*o*-tolylarsinic acid, cream-coloured prisms decomposing at 235—245°; 4-nitro-*o*-tolylarsinic acid, minute needles, m. p. 235—240° (decomp.); 4-amino-*o*-tolylarsinic acid, microscopic needles, decomposing at 222—224° (Benda and Kahn, A., 1908, i, 591, give 180°); 4-nitro-*p*-xylylsarsinic acid, yellow crystals, m. p. 290° (decomp.), which is not identical with the substance obtained by Michaelis (*loc. cit.*) by the nitration of *p*-xylylsarsinic acid; 4-amino-*p*-xylylsarsinic acid (compare Benda and Kahn, *loc. cit.*), colourless platelets, m. p. 213—214° (decomp.); 3-amino-4-hydroxyphenylarsinic acid, decomposing at 290° after darkening and softening at about 220°. H. W.

Silicon-Hydrocarbons with Nuclei containing Halogens, and their Use in Syntheses. GERHARD GRÜTTNER and MARIANNE CAUER (*Ber.*, 1918, **51**, 1283—1292. Compare Grüttner and Krause, A., 1918, i, 132).—An extension of the earlier work. Trichloro-*p*-bromophenylmonosilane reacts with alcohols to form

esters of the type $C_6H_4Br \cdot Si(OR)_3$, which react with magnesium to form organo-metallic derivatives of little value for synthetic purposes. The *methyl* ester, $C_6H_4Br \cdot Si(OMe)_3$, has b. p. $136^\circ/13.5$ mm., $D_4^{16.5} 1.3525$, $D_4^{20} 1.3493$, $n_D 1.50791$, $n_D 1.51210$ and $n_\beta 1.52296$ at 16.5° ; *ethyl* ester, b. p. $149-150^\circ/12$ mm., $D_4^{16.6} 1.2276$, $D_4^{20} 1.2244$, $n_D 1.48872$, $n_D 1.49247$, $n_\beta 1.50206$ at 15.4° ; *propyl* ester, b. p. $175-176^\circ/14$ mm., $D_4^{18.8} 1.1564$, $D_4^{20} 1.1553$, $n_D 1.48144$, $n_D 1.48497$, $n_\beta 1.49386$, $n_\gamma 1.50129$ at 16.6° ; *isobutyl* ester, b. p. $190-191^\circ/14$ mm., $D_4^{17.2} 1.0949$, $D_4^{20} 1.0923$, $n_D 1.47531$, $n_D 1.47865$, $n_\beta 1.48698$, and $n_\gamma 1.49424$ at 14.9° (all densities are reduced to vacuum standard).

The magnesium compound of *p*-bromophenyltriethylmonosilane (*loc. cit.*) reacts badly with formaldehyde, smoothly with acetaldehyde (not paraldehyde), and tolerably well with higher aldehydes to form alcohols of the type $SiEt_3 \cdot C_6H_4 \cdot CHR \cdot OH$; the *ethanol* has b. p. $173-174^\circ/14.5$ mm., $D_4^{19.5} 0.9601$, $D_4^{20} 0.9596$, $n_D 1.51404$, $n_D 1.51822$, $n_\beta 1.52885$, $n_\gamma 1.53810$ at 17.2° ; the *propanol* has b. p. $185^\circ/16.5$ mm., $D_4^{17.0} 0.9603$, $D_4^{20} 0.9575$, $n_D 1.51243$, $n_D 1.51661$, $n_\beta 1.52734$ at 18.0° ; the *n-butanol* has b. p. $199-201^\circ/21$ mm., $D_4^{14} 0.9546$, $D_4^{20} 0.9491$, $n_D 1.50373$, $n_D 1.50754$, $n_\beta 1.51737$; the *isobutanol* has b. p. $190-192^\circ/18$ mm., $D_4^{17.5} 0.9535$, $D_4^{20} 0.9512$, $n_D 1.50820$, $n_D 1.51212$, $n_\beta 1.52231$ at 19.2° . By heating with fuming hydrochloric acid in a sealed tube at 90° , the ethanol gives a good yield of triethylsilicol, b. p. $70.5^\circ/16.5$ mm., $D_4^{19.7} 0.8650$, $D_4^{20} 0.8647$, $n_D 1.43393$, $n_D 1.43639$, $n_\beta 1.44228$, $n_\gamma 1.44675$ at 16.5° .

The magnesium compound of *p*-bromophenyltriethylmonosilane reacts with silicon tetrachloride in ethereal solution to form *trichloro-p-triethylsilylphenylmonosilane*, $SiEt_3 \cdot C_6H_4 \cdot SiCl_3$, b. p. $173-176^\circ/13.5$ mm., a colourless, highly refractive oil which has an offensive odour, fumes in air, and is at once hydrolysed by water. It reacts with magnesium ethyl bromide in ether to form *bis-p-triethylsilylbenzene*, $C_6H_4(SiEt_3)_2$, b. p. $195-196^\circ/16.5$ mm., $D_4^{17.6} 0.8989$, $D_4^{20} 0.8967$, $n_D 1.50555$, $n_D 1.50942$, $n_\beta 1.51945$, $n_\gamma 1.52788$ at 15.7° , a colourless, mobile, not unpleasantly odorous liquid, which is converted by bromination in the presence of an iron catalyst into *p*-dibromobenzene and bromotriethylmonosilane.

The interaction of magnesium *p*-bromophenyl bromide and phenyltrichloromonosilane in ether leads to the formation of *phenyl-p-bromophenyl*dichloromonosilane, $C_6H_4Br \cdot SiPhCl_2$, b. p. $199-200^\circ/14$ mm., $D_4^{18.5} 1.5019$, $D_4^{20} 1.5005$, $n_D 1.60294$, $n_D 1.60921$, $n_\beta 1.62531$, $n_\gamma 1.63953$ at 19° , which is converted by ethyl alcohol into the *diethoxy*-compound, $C_6H_4Br \cdot SiPh(OEt)_2$, b. p. $201^\circ/17$ mm., $D_4^{21.5} 1.2474$, $D_4^{20} 1.2488$, $n_D 1.54525$, $n_D 1.55031$, $n_\beta 1.56322$, $n_\gamma 1.57467$ at 19° , and *bisethoxyphenyl-p-bromophenyldisiloxane*, $(C_6H_4Br \cdot SiPh \cdot OEt)_2O$, b. p. $317-318^\circ/20$ mm., $D_4^{23} 1.3350$, $D_4^{20} 1.3369$, $n_D 1.57867$, $n_D 1.58437$, $n_\beta 1.59895$, $n_\gamma 1.61146$ at 18.6° . *Phenyl-p-bromophenyldiethylmonosilane*, $C_6H_4Br \cdot SiPhEt_2$, b. p. $203-203.5^\circ/13.5$ mm., $D_4^{19.7} 1.2156$, $D_4^{20} 1.2153$, $n_D 1.57794$, $n_D 1.58351$, $n_\beta 1.59781$, $n_\gamma 1.61035$ at 17.9° , and *phenyl-p-ethylphenyldiethylmonosilane*, $C_6H_4Et \cdot SiPhEt_2$, b. p. $169-170^\circ/14$ mm., $D_4^{19.0} 0.98403$, $D_4^{20} 0.98310$, $n_D 1.55716$, $n_D 1.56225$

n_D 1.57559, n_T 1.58713 at 16.8° , are obtained by the interaction of magnesium ethyl bromide and phenyl-*p*-bromophenyldichloromonosilane in ethereal solution, the product after distillation of the ether being heated at about 140° for three hours and then decomposed in the usual manner. Similarly, the product from magnesium ethyl bromide and trichloro-*p*-bromophenylmonosilane, after being heated at 180° for ten hours and then decomposed, yields *p*-ethylphenyltriethylmonosilane, b. p. $117-118^\circ/18$ mm., $D_4^{18.2}$ 0.8969, D_4^{20} 0.8950, n_D 1.50272, n_D 1.50671, n_B 1.51697, n_T 1.52583 at 20.7° . C. S.

Organic Lead Compounds. VIII. Mixed Lead Aryl Alkyls of the Type $PbArR_3$. GERHARD GRÜTTNER and GERTRUD GRÜTTNER (*Ber.*, 1918, 51, 1293—1298).—Such substances are obtained in accordance with the equation $PbR_2X + MgArX = PbArR_3 + MgX_2$, where X is a halogen atom; the diaryl hydrocarbons which are formed as by-products can be removed by freezing or by fractional distillation. Lead aryl trialkyls are colourless, refractive, faintly odorous oils which in the presence of air and in diffuse daylight do not decompose in the course of many months. They decompose above 200° with the separation of lead, and by treatment with bromine in ether at -75° lose the aromatic group, and sometimes also an alkyl group to a slight extent, lead trialkyl bromides and lead dialkyl dibromides being formed. The latter is the main product in the case of lead benzyl triethyl.

The following are described. *Lead phenyl trimethyl*, b. p. $104^\circ/13$ mm., $D_4^{23.7}$ 1.7342, D_4^{20} 1.7376, n_D 1.5753, n_D 1.5816, n_B 1.5988, n_T 1.6138 at 23.7° ; *lead p-tolyl trimethyl*, b. p. $118-119^\circ/13$ mm., D_4^{20} 1.6826, $D_4^{21.5}$ 1.6812, n_D 1.5672, n_D 1.5732, n_B 1.5895, n_T 1.6039 at 20.0° ; *lead o-tolyl trimethyl*, b. p. $117.5-118^\circ/13$ mm., $D_4^{21.4}$ 1.7395, D_4^{20} 1.7408, n_D 1.5734, n_D 1.5793, n_B 1.5954, n_T 1.6095 at 21.4° ; *lead phenyl triethyl*, b. p. $135^\circ/12$ mm., $D_4^{21.1}$ 1.5920, D_4^{20} 1.5931, n_D 1.5698, n_D 1.5757, n_B 1.5917, n_T 1.6057 at 21.1° ; *lead p-tolyl triethyl*, b. p. $154.0^\circ/13$ mm., $D_4^{24.8}$ 1.5237, $D_4^{22.0}$ 1.5262, D_4^{20} 1.5281, n_D 1.5629, n_D 1.5686, n_B 1.5842, n_T 1.5979 at 22.0° ; *lead o-tolyl triethyl*, b. p. $153.5^\circ/13$ mm., $D_4^{21.5}$ 1.5839, D_4^{20} 1.5853, n_D 1.5682, n_D 1.5740, n_B 1.5897, n_T 1.6035 at 21.5° ; *lead benzyl triethyl*, b. p. $149-150.5^\circ/13$ mm., D_4^{23} 1.5374, $n_D^{21.4}$ 1.5843, appears to decompose slightly during distillation, some dibenzyl being formed.

Lead α -naphthyl triethyl loses naphthalene at its b. p. $176^\circ/13$ mm. *Lead benzyl trimethyl* decomposes at 124° . C. S.

Organic Lead Compounds. IX. Lead Triphenyl Haloids. GERHARD GRÜTTNER (*Ber.*, 1918, 51, 1298—1303).—An ethereal suspension of lead tetraphenyl in ether reacts with bromine at about -75° to form essentially a mixture of unchanged material and lead diphenyl dibromide, only about 10% of lead triphenyl bromide being formed. This result is doubtless to be attributed to the easy solubility of the monobromide and the sparing solubility of lead tetraphenyl, in consequence of which the first, when formed, is more readily attacked than the latter. When pyridine

at -50° is used instead of ether (compare Krause, A., 1918, i, 415), an almost quantitative yield of *lead triphenyl bromide*, PbPh_3Br , colourless needles, m. p. 166° , is obtained. It is converted into the *iodide*, PbPh_3I , pale yellow prisms, m. p. 142° , by aqueous potassium iodide, and into the *oxide* by cold 10% aqueous alkali hydroxide. The oxide is converted quantitatively into the *chloride*, PbPh_3Cl , colourless needles or prisms, m. p. 206° , by 15% hydrochloric acid at the ordinary temperature, and from a concentrated alcoholic solution of the latter, hydrogen sulphide precipitates the *sulphide*, $(\text{PbPh}_3)_2\text{S}$, as a white precipitate. C. S.

Physiological Chemistry.

The Consumption of Oxygen and Production of Carbon Dioxide in the Blood of Dogs. I. L. BERCZELLER (*Biochem. Zeitsch.*, 1918, **90**, 294—301).—Sterile blood was kept under mercury or paraffin at 38°, and when fresh, and after keeping for various intervals, the oxygen and carbon dioxide were estimated by Barcroft's method. The production of carbon dioxide was generally found to be greater than the oxygen consumption. Similar experiments were carried out in the presence of dextrose. Here, again, there was no direct relationship between oxygen consumption and carbon dioxide production. There was a much larger oxygen consumption and carbon dioxide production than in normal blood.

S. B. S.

Analysis of Blood Gases. II. Hæmoglobin as an Indicator. The Theory of Indicators. H. STRAUB and KLOTHILDE MEIER (*Biochem. Zeitsch.*, 1918, **90**, 305—336).—There is a discontinuity of the curve expressing the amount of carbon dioxide taken up by the blood (hæmolysed by saponin freezing, etc.) plotted against the carbon dioxide tension. This discontinuity does not follow the ordinary laws of mass action, but begins when $p_H = 7.0$, at which point one molecule of carbon dioxide is taken up by one molecule of hæmoglobin. This indicates that when $p_H > 7.0$ the hæmoglobin molecules carry a negative charge, which they lose as soon as $p_H = 7$. When $p_H = 6.39$, a second point of discontinuity is reached in the curve, which indicates that at this point the hæmoglobin molecules acquire a positive charge. These phenomena are explained in reference to the charges carried by the colloidal particles, and not by the laws of mass action, for the position of the bends in the curve depends also on the presence of other ions than those of hydrogen. Univalent anions and cations, and bivalent cations exert no influence on the position of the bend; trivalent anions shift the position of the first bend from $p_H = 7.00$ to $p_H = 6.80$,

and are without action on the position of the second bend. Tervalent cations also exert a strong influence on the position. The application of these facts to the use of hæmoglobin as an indicator is discussed.

S. B. S.

The Influence of Narcotics on the Permeability of Blood-corpuscles for Dextrose and Carbamide. GERTRUD KATZ (*Biochem. Zeitsch.*, 1918, **90**, 153—165).—The entrance of dextrose into human blood corpuscles is not inhibited by the narcotics heptyl alcohol and thymol. The entrance of carbamide into ox-corpuscles is delayed by thymol.

S. B. S.

The Part Played by Acid in Carbohydrate Metabolism. III. Acid and the Glycogen of the Muscles. H. ELIAS and E. SCHUBERT (*Biochem. Zeitsch.*, 1918, **90**, 229—243).—The glycogen content of the muscles of dogs' legs differs, the right from the left, by about 2—3% in the mean. Interarterial injection of lactic acid over several hours does not reduce to any appreciable extent the amount of glycogen; the muscle glycogen appears to be far more resistant to external stimuli than does the liver glycogen.

S. B. S.

Salivary Amylase. I. A Preliminary Experimental Study of its Stability in Saliva. ROLLIN C. MYERS and LEONARD C. SCOTT (*J. Amer. Chem. Soc.*, 1918, **40**, 1713—1716).—Salivary amylase in sterilised saliva without preservative is found to be relatively stable for a year. The relative stability may vary from practically no change to that of more than 50% of its former amylolytic activity, the variation depending probably on slight differences in the composition of the saliva.

The causes which lower the stability of salivary amylase in saliva are not solely the degrading action of bacteria, mould spores, yeast plants, and special preservatives. The inherent chemical weakness of the enzyme molecule must be taken into account, which weakness may be increased by the maintenance of temperatures from 18° to 30°, by diffused light and by compounds in the saliva.

Salivary amylase in saliva is relatively stable for a year when preserved with toluene, thymol, and chloroform. Toluene has the least destructive action on the enzyme, and thymol and chloroform follow in order.

Saliva may be kept for two and a-half years under the ordinary laboratory conditions without preservative, and may still show a form of amylolytic activity.

H. W.

The Presence of Food Accessories in Urine, Bile, and Saliva. A. M. MUCKENFUSS (*J. Amer. Chem. Soc.*, 1918, **40**, 1606—1611).—As a result of a series of experiments on pigeons with acute symptoms of polyneuritis, the author is led to the conclusion that the antineuritic vitamine is probably present in comparatively small quantity in clean, fresh, filtered bile from the

bladder of the ox, and that traces of it appear to be present in fresh filtered human urine. H. W.

Fischer's Theory of Water Absorption in Œdema. W. J. CROZIER (*J. Amer. Chem. Soc.*, 1918, **40**, 1611—1612. Compare Fischer, A., 1918, i, 129, 130, 131; Henderson and Cohn, *ibid.*, i, 316).—The author has carried out a series of experiments on the intracellular acidities in the tissues of three species of sponges, one echinoderm, and a nudibranch mollusc. The observations made increase the difficulties in the way of accepting Fischer's conception of water metabolism, since they indicate a range of intracellular acidities, in animal tissues, within which it is known that no significant protein swelling occurs, and since they show that an intracellular acidity even remotely approaching that at which significant swelling might be possible is irreversibly associated with natural death. H. W.

The Storage and Excretion of Arsenic after Administration by Salvarsan in Serum and Water. HANS BERGMANN (*Biochem. Zeitsch.*, 1918, **90**, 348—360).—The author investigated the rate of excretion of arsenic excreted in the urine of man after administration of neosalvarsan in serum (human) and in aqueous solutions. In the latter case the excretion is much greater. Experiments are quoted which tend to show that the salvarsan undergoes chemical change more rapidly in aqueous solution than in serum. A series of experiments is also described, in which the accumulation of arsenic in the organs of rabbits after administration of salvarsan was investigated. They tend to indicate a greater accumulation after administration of the drug in serum. S. B. S.

Chemistry of Vegetable Physiology and Agriculture.

A Bacterium present in Water and in Bitter Wines which is capable of Dehydrating Glycerol. A New Reaction for Glycerol. E. VOISENET (*Ann. Inst. Pasteur*, 1918, **32**, 476—510. Compare A., 1914, i, 462).—The new bacterium, termed *Bacillus amaracrylus*, is related to *B. coli* and *B. typhosus*, but is not pathogenic. When cultivated in dextrose solution, it forms carbon dioxide and hydrogen, like *B. coli*, but it does not form indole from tryptophan. Inoculation of a medium containing glycerol with the new bacterium results in the production of acraldehyde, which is its characteristic reaction. H. W. B.

The Inter-relationship of certain processes in Metabolism of *Bacillus coli communis*. FRITZ VERZER (*Biochem. Zeitsch.*, 1918, **91**, 1—45).—Three main series of investigations were

instituted: (1) The influence of certain poisons on the different processes, (2) the influence of one metabolism product on the formation of others, (3) the regulation of the formation of a product by its own accumulation. The processes investigated were (a) gas formation from dextrose, (b) acid formation from dextrose and lactose, (c) indole formation, (d) reducing action on dyes, (e) multiplication of the bacteria.

(1) Protoplasmal poisons, phenol, formaldehyde, and mercuric chloride inhibit all the processes in about the same concentration. Crystal-violet shows slight inhibition of gas formation, but strong inhibition of reducing processes. The respiratory poison, potassium cyanide, inhibits strongly gas formation and still more strongly reduction processes and indole formation in concentrations in which the acid formation is not affected. The narcotic, chloroform, inhibits respiration, but not as strongly as potassium cyanide; in contrast to the latter, it also inhibits acid formation. Alcohol acts, but less strongly, like chloroform. The author draws the conclusion that the only really essential vital process is the formation of acid from dextrose.

(2) From the study of the presence of acid on indole formation it was found that the latter is inhibited entirely by the presence of acids, and is only normally produced from proteins or peptones by the bacteria in the absence of dextrose; scission of this by the bacteria produces acid to inhibit indole formation.

(3) The influence of the presence of acids and alkalis on the further formation of acids by the bacteria was investigated. It was found that when the acid in the culture medium reached a certain concentration, further formation of acid was inhibited, and also further formation of carbon dioxide, and multiplication of bacteria. If sugar insufficient to produce the amount of acid necessary for inhibitions is present, alkali formation sets in, until the medium attains a slightly alkaline reaction, when further formation of alkali is inhibited. The formation takes place only in presence of oxygen. From acid (except formic acid) no gas is formed either after reaching its maximum concentration or during formation of alkali. Inhibition of oxidation causes a compensatory increased production of acid.

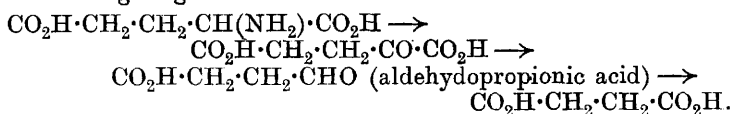
S. B. S.

Phytochemical Reductions. XIII. Asymmetrical Reduction. Conversion of Racemic Valeraldehyde (*dl*- α -Methylbutaldehyde) into *l*-Amyl Alcohol. C. NEUBERG and M. RINGER (*Biochem. Zeitsch.*, 1918, **90**, 388—394).—The amyl alcohol produced from *dl*- α -methylbutaldehyde by a sugar-yeast fermentation mixture is laevorotatory.

S. B. S.

The Method of Formation of Succinic Acid in Nature. III. Conversion of Aldehydopropionic Acid into Succinic Acid by Yeast. C. NEUBERG and M. RINGER (*Biochem. Zeitsch.*, 1918, **91**, 131—136).—By means of maceration juice, and in absence of air, aldehydopropionic acid can be converted into succinic acid.

The conversion of glutamic acid into succinic acid follows, therefore, the following stages:



All these stages except the first, which takes place, as far as investigations have gone, only in the living cell, can be accomplished by purely enzymatic reactions.

S. B. S.

Physiological Investigation of a New Yeast which Flourishes in Tanning Liquors. TÔICHI ASAI (*J. Coll. Sci. Imp. Univ. Tokyo*, 1918, **39** (7), 1—42).—The new yeast, designated *Mycoderma tannica*, forms dark brown or brownish-black spots on leather undergoing the tanning process. The isolated yeast can be cultivated in a solution containing dextrose or lævulose or other carbohydrate, and an ammonium salt or amino-acid as a source of nitrogen. It does not readily grow in a dilute pure tannin solution, but when dextrose and aspartic acid are also present, rapid decomposition of the tannin occurs, owing to the excretion of tannase into the surrounding medium. The growth of the yeast is attended by the production of small quantities of alcohol and carbon dioxide, indicating the presence of zymase. Addition of tannin to the medium increases slightly the alcoholic fermentation.

H. W. B.

Kinetics of the Cell-free Fermentation [by Zymase].

OTTO MEYERHOF (*Zeitsch. physiol. Chem.*, 1918, **102**, 185—225).—The addition of sugar to an extract of dried yeast containing zymase, but free from cells, is succeeded by a period of quiescence, during which no sign of fermentation is observable. The interval which elapses between the addition of the sugar and the first appearance of fermentation is termed the "induction period." The duration of the induction period is determined by various factors; it is shorter for sucrose than for either dextrose or lævulose; it can be shortened by previously warming the sugar solution with disodium hydrogen phosphate or by grinding the dried yeast with glass powder. The presence of a small amount of hexose phosphate abolishes the induction period.

The rate of fermentation is dependent on the amount of free phosphate present. Increasing the amount of disodium hydrogen phosphate reduces the rate at which the velocity of fermentation increases, but the maximum velocity eventually attained is higher than in the absence of free phosphate until a certain maximum amount of the phosphate is reached; further addition of the phosphate then reduces the maximum velocity of fermentation attainable. The addition of other salts, such as sodium chloride, produces similar effects on the velocity of fermentation. The free phosphate functions, therefore, as a salt as well as exerting its specific zymase-activating action.

Hexose phosphate exerts an accelerating action on fermentation in proportion to its concentration, due to the decomposition of the ester itself. Fermentation is accelerated also by the addition of co-ferment in the form of boiled yeast juice; the extent to which it is affected depends on the concentration, and not on the absolute quantity of the co-ferment present in relation to zymase.

The inhibiting influence of narcotics on the fermentation of dextrose by zymase is somewhat intensified by the addition of salts.

H. W. B.

Rôle of the Phosphate in Alcoholic Fermentation.

HANS EULER and S. HEINTZE (*Zeitsch. physiol. Chem.*, 1918, 102, 252—261).—The esterification of phosphoric acid by dried yeast in the presence of a protoplasmic poison, such as phenol, is related to the amount of water remaining in the yeast after the drying process. The maximum esterification is observed when dried yeasts containing from 10 to 15% of moisture are employed. Increasing the quantity of yeast used in the individual experiments appears to occasion a much greater increase in the amount of hexose phosphate produced.

H. W. B.

Fumaric Acid Fermentation of Sugar. C. WEHNER (*Ber.*, 1918, 51, 1663—1668).—*Aspergillus fumarius* smoothly ferments relatively large quantities of sugar, yielding, in addition to a little citric acid, fumaric acid in the free state; the solution turns Congo-paper blue and dissolves calcium carbonate. Oxygen is necessary and, for continuous fermentation, calcium carbonate. Thus 20 grams of sugar (20% solution) and 2.87 grams (dry weight) of *Aspergillus fumarius* dissolve 15 grams of calcium carbonate and produce about 33 grams of calcium salts consisting chiefly of the sparingly soluble normal calcium fumarate, but containing also varying quantities of the easily soluble hydrogen fumarate, about 4% of calcium citrate, and the calcium salt of another, unidentified acid. The sugar is fermented completely, and 60—70% of it is converted into acids. The optimum temperature is about 22°, the maximum about 30°.

C. S.

Behaviour of Organic Compounds in Plants. X. G. CIAMICIAN and C. RAVENNA (*Gazzetta*, 1918, 48, i, 253—304. Compare A., 1918, i, 473).—The first part of this paper, dealing with the action of certain compounds on the germination and development of plants, has been already abstracted.

The second part describes further investigations on the oxidation of organic compounds by the agency of enzymes contained in spinach leaves. The results of experiments in an atmosphere of carbon dioxide show that the disappearance of certain substances in an atmosphere of oxygen as a result of the action of such enzymes is due to an oxidation process.

In an atmosphere of carbon dioxide, saligenin is converted into the polyanhydride saliretin, this change being effected more

promptly by apple pulp than by spinach leaves. Ethyl alcohol and mannitol are not sensibly oxidised. Acetaldehyde, which undergoes little auto-oxidation in an atmosphere of oxygen, is not affected by the presence of the enzyme. The oxidation of acetone to formic and acetic acids under the influence of light is catalysed by the presence of the enzyme. Of the three amino-acids examined, glycine, alanine, and asparagine, only the last is oxidised by the enzyme in an atmosphere of oxygen, no change occurring in carbon dioxide. Cinnamic acid is not oxidised at the double linking, only minimal traces being transformed into the isomeric *isocinnamic* acid; this isomerisation does not occur in carbon dioxide. Of the alkaloids examined, caffeine and strychnine remain unchanged, whereas morphine, quinine, and cinchonine are largely oxidised.

The enzymes of spinach leaves are also able to determine certain other reactions. Thus, in oxygen, dextrose is completely oxidised, probably to carbon dioxide, whilst in carbon dioxide it yields a substance giving dextrose on hydrolysis with acid. Further, in either oxygen or carbon dioxide, tartaric acid undergoes change, partly into a compound yielding tartaric acid under the action of emulsin.

The results of the experiments described in the third part of the paper show that, when inoculated into the living plant (maize), pyridine and nicotine are partly eliminated through the leaves, the transformation of further quantities by the plant being also indicated, but not definitely proved.

T. H. P.

The Influence of Immersion in certain Electrolytic Solutions on Permeability of Plant Cells. MAUD WILLIAMS (*Ann. Bot.*, 1918, **32**, 591—599).—Cells of London Pride (*Saxifraga umbrosa*) petioles, after immersion in solutions of certain electrolytes, were found to be permeable to a 0.2% solution of ferric chloride, the entrance of the ferric chloride being indicated by formation of a blue colour with the tannin contained in these cells. The time of immersion in a given solution necessary to produce this abnormal permeability varied with the electrolyte and its concentration. In the cases of aluminium and potassium chlorides, and potassium and barium nitrates, the results obtained could be expressed approximately by the equation

$$\log T = K - A(\log C + 1),$$

where T is the time of immersion in the solution of the electrolyte needed to produce the abnormal permeability, C is the concentration in gram-mols. per litre, K is an independent constant, and A a constant depending on the electrolyte used. Abnormal permeability with respect to ferric chloride was not always accompanied by permeability to the rose-coloured pigment frequent in the sap of the cells.

W. G.

The Occurrence of Melezitose in a Manna from the Douglas Fir. C. S. HUDSON and S. F. SHERWOOD (*J. Amer. Chem. Soc.*, 1918, **40**, 1456—1460).—A sample of manna from

the Douglas fir yielded about 50% of pure crystalline melezitose, and there is evidence that it contained sucrose and some reducing sugar, probably a mixture of dextrose with a smaller quantity of lævulose. The composition of the sample of dry manna was approximately: melezitose 75—83%, sucrose 2·9%, reducing sugars 11·5%. At present, the only other known natural source of melezitose in any quantity is the Tarkestan manna (Tarandjabiné), which is, however, considerably inferior to the Douglas fir product in point of yield.

H. W.

Occurrence of Allantoin in the Rhizome of *Symphytum officinale* and other Borraginaceæ. ALFRED VOGL (*Pharm. Post.*, 1918, **51**, 181—184; from *Chem. Zentr.*, 1918, ii, 36).—Large quantities of allantoin crystals, in the form of monoclinic prisms, are found in the rhizome of *Symphytum officinale*. The author has also succeeded in identifying allantoin crystals in the sections of the rhizome and has determined their distribution in the tissue. Crystallisation in the sections is best effected by pouring on them alcohol containing acetic acid (20%), covering with a cover-glass, and sealing with paraffin. The allantoin content of the rhizome of *S. officinale* varies with the time of year; it is at a maximum from autumn to early spring, at a minimum in the height of summer. The rhizomes of *S. tuberosum*, *S. cordatum*, *S. caucasicum*, and other *Borraginaceæ* appeared to be free from allantoin, possibly owing to unfavourable supply of material.

H. W.

Action of Ammonium Salts on Plants. I. H. G. SÖDERBAUM (*Kungl. Landtbruks-Akad. Handlingar*, 1917, **56**, 537—561; from *Physiol. Abstr.*, 1918, **3**, 351).—This paper reports experiments with small grains and potatoes grown in pots, using ammonium salts as fertilisers; sodium nitrate was used in part for control purposes. The favourable influence of these salts on the total yield ranks as follows: diammonium hydrogen phosphate, ammonium carbonate, sulphate, nitrate, sodium nitrate, ammonium chloride. The phosphate gave a crop four times as large as an equivalent amount of the sulphate; the chloride proved very disadvantageous. Up to a certain limit, the addition of ammonium sulphate gave a progressively increased yield, but when the limit had been passed, there was a marked decrease. The adverse action of an excess of the salt was not the same in the case of each plant. Rye and potatoes were least sensitive in this respect, and wheat and barley most so, whilst oats occupied an intermediate position. Where there is neither soil acidity nor a deficiency of calcium, ammonium sulphate may be used to advantage in the field, as the amount applied in practice does not reach the limit where toxicity manifests itself.

H. W. B.

Organic Chemistry.

Methane. WILLIAM MALISOFF and GUSTAV EGLOFF (*J. Physical Chem.*, 1918, **22**, 529—575).—A summary is given of the work which has been published, from all sources, on the physical and chemical properties of methane, and a number of important problems requiring investigation are enumerated. [See *J. Soc. Chem. Ind.*, 1919, 35A.] E. H. R.

Organic Chemical Reagents. II. Amylene. *tert*-Amyl Alcohol. ROGER ADAMS, O. KAMM, and C. S. MARVEL (*J. Amer. Chem. Soc.*, 1918, **40**, 1950—1955).—Dehydration of primary alcohols by sulphuric acid generally proceeds less satisfactorily as the molecular weight of the alcohol increases. Amylene may, however, be satisfactorily obtained from commercial amyl alcohol under the following conditions. Amyl alcohol (1.5 litres) and concentrated sulphuric acid (100 c.c.) are heated to vigorous boiling under a reflux condenser in which the water is maintained at such a temperature (60—90°) as to allow a considerable amount of vapour to distil out of the apparatus; the top of the condenser is connected with a second, efficiently cooled condenser, attached so as to permit downward distillation. The heating requires a maximum time of about eight hours. At first, water and amyl alcohol pass over, whilst subsequently amylene distils. The distillate is washed with sodium hydroxide to remove sulphur dioxide and the amylene isolated by fractionation. It appears to consist of β -methyl- Δ^{α} -butylene and β -methyl- Δ^{β} -butylene containing only a negligible amount of γ -methyl- Δ^{α} -butylene. The residue in the original flask contains amyl alcohol and *iso*amyl ether, which are recovered by distillation with steam and subsequent fractionation. About 250 c.c. of amylene, 400 c.c. of *iso*amyl ether, and 500 c.c. of amyl alcohol are obtained from 1500 c.c. of the latter.

Larger amounts of amylene are more conveniently obtained by the pyrogenic-catalytic method, using aluminium oxide as catalyst at 500—540°. A suitable electrically heated furnace is fully described. The general procedure is similar to that indicated by Ipatieff (A., 1903, i, 593). The yield of amylene is 70—80% of the theoretical, and the product is about 98—99% pentene. The catalyst retains its activity over lengthy periods.

tert-Amyl alcohol is prepared by the gradual addition of amylene to a mixture of concentrated sulphuric acid and ice. The product is diluted with ice-water (after removal of any unchanged amylene), rendered alkaline with sodium hydroxide, and distilled. 275—300 Grams of a product, b. p. 100—103°, may be obtained from 325 grams of amylene. H. W.

Geometrical Isomerism. A. E. LACOMBLÉ (*Chem. Weekblad*, 1918, **15**, 605—610).—The inconsistencies which are introduced

by the attempts to explain the existence of the *cis*- and *trans*-isomerides of ethylenic compounds of the type $(A,B)C=C(A,B)$ by the theories of Werner and Stark are pointed out. All such theories set out to explain how the existence of the double bond prevents free rotation of the two doubly-linked carbon atoms about the line joining their centres. The explanations of Werner and of Stark are shown to be inconsistent with the hypotheses which they put forward as to the nature of the atoms and the mechanism by which the atoms are linked together. The author points out that it is hopeless to attempt to base an hypothesis of the structure of the benzene ring, for example, on theories which are inadequate to explain the mechanism of the double bond. S. I. L.

Derivatives of Trihalogeno-*tert*.-butyl Alcohols. II. The Propionic and Butyric Esters of Tribromo-*tert*.-butyl Alcohol (Brometone). T. B. ALDRICH (*J. Amer. Chem. Soc.*, 1918, **40**, 1948—1950. Compare Aldrich and Beckwith, A., 1917, i, 77).— β -Tribromomethylpropan- β -ol is converted into the corresponding *propionate*, white crystals, m. p. 27° , by the action of propionyl chloride. The similarly prepared *butyrate* is an oil, b. p. 144 — $145^{\circ}/13$ — 14 mm. Both are comparatively inactive pharmacologically, due probably to their not being decomposed into soluble constituents having a typical physiological action and are rather slowly absorbed. H. W.

Glyceryl Methyl Ether Dinitrate (α -Methylin Dinitrate). DAVID TREVOR JONES (T., 1919, **115**, 76—81).

The Action of Sodium Hydroxide on Carbon Monoxide, Sodium Formate, and Sodium Oxalate. MAITLAND C. BOSWELL and J. V. DICKSON (*J. Amer. Chem. Soc.*, 1918, **40**, 1779—1786).—It has been shown (this vol., ii, 63) that fused sodium oxide is very active in effecting oxidations. It is now demonstrated that at 410 — 430° , carbon monoxide in contact with fused sodium hydroxide is oxidised to carbon dioxide, an equivalent amount of hydrogen being produced at the same time. Sodium formate when fused with sodium hydroxide at 275° , a temperature much below its decomposition temperature, is oxidised almost quantitatively to carbon dioxide in a very short time, an equivalent amount of hydrogen also being formed. Sodium oxalate is similarly oxidised at 290° . In both these cases, it is the water present in the fusion, catalysed by the sodium hydroxide, which is the effective oxidising agent. It is held that the general reaction involving the replacement of the carboxyl group by hydrogen in alkali fusions, for example, in the formation of benzene from sodium benzoate, involves simultaneous oxidation and reduction by the oxygen and hydrogen of water. [See also *J. Soc. Chem. Ind.*, 1919, February.] E. H. R.

Quinonoid Character of Maleic Anhydride. PAUL PFEIFFER and THEODOR BÜTTLER (*Ber.*, 1918, **51**, 1819—1829. Compare Pratt and Perkins, A., 1918, i, 167).—Maleic anhydride is related

to furan in the same manner as quinone to benzene; it may therefore be regarded as a quinone of furan, and, in the present communication, evidence is adduced to show that the formal analogy is reproduced in its properties.

A characteristic property of quinones is their ability to yield more or deeply coloured molecular compounds with aromatic hydrocarbons, amines, phenols, and phenol ethers (A., 1914, i, 551; 1917, i, 205); this property is shared by maleic anhydride, which, although yielding colourless solutions in benzene, toluene, or *m*-xylene, gives coloured solutions with durene, hexamethylbenzene, naphthalene, 2:4:5:2':4':5'-hexamethylstilbene, *o*-tolyl methyl ether, and quinol and dimethylaniline. The influence of substituents in the molecule of the solute and solvent, respectively, is similar in the cases of *p*-benzoquinone and of maleic anhydride. Thus, methylation in the quinone molecule exerts a hypsochromic action on the colour of the quinhydrone; similarly, solutions of citraconic anhydride are less intensely coloured than corresponding solutions of maleic anhydride. Methylation in the benzenoid component produces a deepening of colour in the cases of *p*-benzoquinone and of maleic anhydride. The introduction of an *ortho*-condensed benzene nucleus has a similar influence in each instance, as is proved by the comparison of α -naphthaquinone with *p*-benzoquinone on the one hand and of phthalic anhydride with maleic anhydride on the other. The deepening in colour caused by the introduction of halogen atoms into the quinone molecule is remarkably characteristic; the same effect is produced in the anhydrides, as proved by examination of bromomaleic, dibromomaleic, and tetrachlorophthalic anhydrides. Attempts to isolate the additive compounds of maleic anhydride or its bromo- or methyl derivatives in the crystalline state were not successful, but similar *substances* were readily obtained from tetrachlorophthalic anhydride and durene (long, pale yellow needles) and hexamethylstilbene (orange-coloured, shining leaflets, m. p. 183—184°), respectively.

The effect of alteration in the structure of the anhydride has also been investigated. Succinic anhydride yields colourless solutions in all the media mentioned above, whilst the solutions of itaconic anhydride are much less deeply coloured than those of citraconic anhydride. When dissolved in dimethylaniline, itaconic anhydride is gradually isomerised to citraconic anhydride. On passing from the anhydride to the corresponding acid or its esters, the quinonoid character is largely lost and the solutions are colourless or less intensely coloured, as is shown at the instances of maleic and dibromomaleic acids, of methyl fumarate, and of methyl tetrachlorophthalate. The substance, $\text{CO}_2\text{H}\cdot\text{CBr}\cdot\text{CBr}\cdot\text{CHO}$, scarcely possesses any quinonoid characteristics, but these are more marked with *trans*-dibenzoylethylene. γ -Pyrone and the ketones of the distyryl ketone series are less nearly related to quinone than is maleic anhydride; the former yields completely colourless solutions, whilst those of the latter only show faint colorations.

It was to be expected that imides of the type of maleinimide

would also show quinonoid characteristics; this is actually the case, but solutions of citraconanil and tetrachlorophthalimide are less deeply coloured than those of citraconic and tetrachlorophthalic anhydrides.

Maleic, citraconic, phthalic, and tetrachlorophthalic anhydrides do not exhibit halochromic phenomena when treated with concentrated sulphuric acid, trichloroacetic acid, or tin tetrabromide. Further investigation of this problem has led to the conclusion that the carbonyl groups of the substances which yield quinhydrones and of typical halochromic compounds must differ markedly in their chemical nature.

H. W.

Oxidation of Organic Compounds by Silver Oxide.

ROBERT BEHREND and KARL DREYER (*Annalen*, 1918, 416, 203—225).—It has long been known that many acids and alcohols are oxidised by silver oxide, but hitherto a systematic investigation has not been made of the relation between the constitutions of substances and their tendency to oxidation or of the nature and quantity of the products of oxidation. The present paper deals with these points in the case of the simpler, hydroxylic aliphatic compounds. In order that a substance may be oxidised by silver oxide in alkali hydroxide or ammoniacal solution, it must contain a $\text{:CH}\cdot\text{OH}$ (or CO or C[OH]_2) group combined with two $\cdot\text{CH}_2\cdot\text{OH}$, two $\text{:CH}\cdot\text{OH}$, or two $\cdot\text{CO}_2\text{H}$ groups, or with any two of these three groups. Tartronic, tartaric, dihydroxytartaric, glyceric, mucic, saccharic, and gluconic acids, dextrose, glycerol, and mannitol are thus oxidised. For oxidation in neutral or acid solution, it suffices that the $\text{:CH}\cdot\text{OH}$ group shall be combined with a carboxyl group and also with H , CH_2 , or CH_3 . Glycollic, lactic, malic (and also formic) acids are thus oxidised. Propylene glycol, ethyl alcohol, isopropyl alcohol, and oxalic acid suffer little or no oxidation. In alkali hydroxide solution, substances of the group first mentioned are oxidised rapidly and completely; the rate of oxidation is accelerated, but the relative quantities of the products of oxidation are unaffected by an increased concentration of the alkali hydroxide. In ammoniacal solution, silver oxide oxidises the alkali salts of the acids completely in fifty minutes at 90° . The acids are more easily oxidised in the form of alkali salts than in the form of ammonium salts. An excess of ammonia or of ammonium salt retards the oxidation.

The products of oxidation in alkaline solution contain at most two atoms of carbon, and are never obtained in simple molecular proportions. All the substances with the exception of glycerol yield carbon dioxide as one of the products of oxidation in acid or in alkaline solution. Formic acid is a product of oxidation in alkaline solution, and then only if the oxidisable substance contains a $\text{:CH}\cdot\text{OH}$ group united with a $\text{:CH}\cdot\text{OH}$ or $\cdot\text{CH}_2\cdot\text{OH}$ group as well as with a $\text{:CH}\cdot\text{OH}$, $\cdot\text{CH}_2\cdot\text{OH}$, or $\cdot\text{CO}_2\text{H}$ group. Formic acid may be an intermediate product of oxidation in acid solution, but in such circumstances it undergoes further oxidation. Oxalic

acid is almost always the chief product of oxidation in alkaline solution; in neutral or acid solution, it is formed in much smaller quantity. In neutral solution, malic acid yields malonic acid, and lactic acid and propylene glycol yield acetic acid. C. S.

Tartronic Acid. ROBERT BEHREND and AUGUST PRÜSSE (*Annalen*, 1918, **416**, 233—239).—Tartronic acid has been prepared by eleven investigators, who record eight different m. p.'s between 145° and 185°. The correct value appears to be 156—158° (decomp.). C. S.

Preparation of Gulonolactone. F. B. LA FORGE (*J. Biol. Chem.*, 1918, **36**, 347—349).—To a solution of 150 grams of xylose in 300 c.c. of water, 30 grams of hydrocyanic acid are added, and then a few drops of ammonium hydroxide. The reaction commences at once, and is completed in about six hours at 35°. Slightly more than one equivalent (55 grams) of sulphuric acid diluted with a small amount of water is added to the solution, which is then concentrated at once to a viscous syrup. Hydrolysis of the nitrile takes place, and on cooling and keeping, the lactone crystallises out. The yield after recrystallisation from 60% alcohol amounts to 55 to 60% of the weight of xylose used. H. W. B.

Crystallography and Optical Properties of Three Aldopentoses. EDGAR T. WHERRY (*J. Amer. Chem. Soc.*, 1918, **40**, 1852—1858).—The optical properties of the crystals of the three sugars α -*D*-lyxose, α -*D*-xylose, and β -*D*-arabinose enable them to be readily distinguished, and a determinative table is given for this purpose. For the determination of the refractive indices by the immersion method, suitable mixtures of turpentine oil (n 1.47), clove oil (n 1.53), and α -bromonaphthalene (n 1.66) are used.

α -*D*-Lyxose forms monoclinic, probably sphenoidal, crystals, $a:b:c=1.608:1.1828$; $\beta=62^\circ 10'$; mean refractive index, n 1.541; D^{20} 1.545; molecular refraction, M 30.60.

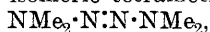
α -*D*-Xylose, rod-shaped, monoclinic, probably sphenoidal, crystals, $a:b:c=1.655:1.1776$; $\beta=62^\circ 55'$; n 1.536; D^{20} 1.525; M 30.67.

β -*D*-Arabinose, rhombic, probably sphenoidal, needles, $a:b:c=1.497:1.0738$; n 1.568; D^{20} 1.605; M 30.61.

Lyxose and xylose are obviously very closely related crystallographically, and β -arabinose, although crystallising in a different system from the others, shows closely similar inter-facial angles, and the three sugars form an essentially isomorphous group. The molecular refractivities are all slightly lower than that calculated from the atomic refractivities, 31.2. The divergence is probably due to some peculiarity of molecular configuration. E. H. R.

Tetramethylammonium Azide. FRANK V. FRIEDLANDER (*J. Amer. Chem. Soc.*, 1918, **40**, 1945—1947).—*Tetramethylammonium azide*, NMe_4N_3 , is prepared by the gradual addition of a solution of tetramethylammonium iodide to an aqueous suspension of a slight excess of silver azide. The crystals belong to the tetragonal system ($a:c=1.07245$). It is a fairly

stable substance which does not explode when struck with a hammer, when ground in a mortar, or when dropped on a hot plate; the dry salt begins to decompose at about 125°. Attempts to transform it into the isomeric tetramethyltetrazone,



have been unsuccessful up to the present.

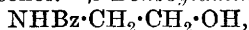
H. W.

Glycosine. ROBERT BEHREND and HERMANN KÖLLN (*Annalen*, 1918, **416**, 230—233).—In addition to glyoxaline, very small quantities of glycosine are obtained by the action of ammonia on glyoxal. The yield of glycosine is considerably increased by the following procedure. In a tall cylinder are placed 20 c.c. of nitric acid, D 1·4, containing ten to fifteen drops of fuming nitric acid, 25 c.c. of water, and 25 c.c. of paraldehyde, the three liquids being introduced with as little intermixture as possible. The cylinder is immersed in water, the level of which is higher than that of the liquids in the cylinder. When the liquids have intermixed after some days and the evolution of gas has ceased, the mixture is repeatedly evaporated with water to remove volatile acids as completely as possible, and the residual syrup is diluted to 50 c.c. with water, producing an approximately 20% solution of glyoxal. One-half of this solution is evaporated until the temperature is 120°, 25—30 grams of ammonium acetate which has been heated at this temperature are gradually added, the resulting brownish-black liquid is dried at 100—110° and treated with water. The black residue of crude glycosine is dried in air and then at 70°, dissolved in warm 35% hydrochloric acid (which is added drop by drop), the solution is diluted with water, boiled with animal charcoal (free from iron), filtered after keeping for twenty-four hours in the warm, the brown filtrate is boiled again with animal charcoal, and the colourless filtrate is neutralised by ammonia, whereby glycosine is obtained in 42·5% yield.

A modification of Pinner's method of preparing trichlorolactic acid from chloral is described.

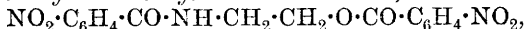
C. S.

β-Aminoethyl Alcohol and its Derivatives. SIGMUND FRÄNKEL and MARTHA CORNELIUS (*Ber.*, 1918, **51**, 1654—1662).—The following derivatives have been prepared to facilitate the identification of the amino-alcohol. *β-Benzoylaminoethyl alcohol*,



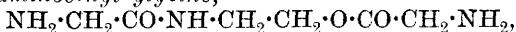
prepared by boiling an alcoholic solution of the dibenzoyl derivative with the quantity of solid potassium hydroxide calculated to eliminate one benzoyl group, forms colourless leaflets, m. p. 66—67°. *β-Acetylaminoethyl acetate*, $\text{NHAc}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OAc}$, b. p. 103°/0·049 mm., is obtained by boiling β-aminoethyl alcohol with acetic anhydride. *β-Acetylaminoethyl alcohol*, prepared from the amino-alcohol and acetyl chloride at 0°, forms colourless needles, m. p. 63—65°. *β-Naphthalenesulphonylaminoethyl alcohol*, $\text{C}_{10}\text{H}_7\cdot\text{SO}_2\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$, asbestos-like crystals, m. p. 86—87°, is obtained by adding *N*-sodium hydroxide to an ethereal solution

of β -naphthalenesulphonyl chloride (2 mols.) and β -aminoethyl alcohol (1 mol.), and subsequently acidifying the aqueous solution. *β -m-Nitrobenzoylaminoethyl m-nitrobenzoate*,



colourless needles, m. p. 152—153°, obtained by heating β -aminoethyl alcohol (1 mol.) and *m*-nitrobenzoyl chloride on the water-bath, is reduced by the calculated quantity of tin and hydrochloric acid to *β -m-aminobenzoylaminoethyl m-aminobenzoate hydrochloride*, $\text{C}_{16}\text{H}_{17}\text{O}_3\text{N}_3\cdot 2\text{HCl}$, crystals, m. p. 232°. *β -p-Nitrobenzoylaminoethyl p-nitrobenzoate*, yellow needles, m. p. 188—189°, and *β -p-aminobenzoylaminoethyl p-aminobenzoate*, crystals, m. p. 206°, are obtained by similar methods. *β -Phenylcarbamidoethyl phenylcarbamate*, $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{CO}\cdot\text{NHPh}$, colourless crystals, m. p. 190—191°, is obtained by adding phenylcarbimide drop by drop to cold β -aminoethyl alcohol, and then heating the mixture in a sealed tube at 100°. *β -Aminoethyl hydrogen sulphate*, $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{SO}_3\text{H}$, colourless crystals, m. p. 230°, is obtained from the amino-alcohol and fuming sulphuric acid in a freezing mixture.

β -Glycylaminoethyl glycine,



obtained by adding chloroacetyl chloride (2 mols.) to a chloroform solution of β -aminoethyl alcohol (1 mol.) at 0° in the presence of lead carbonate, warming the mixture for a moment on the water-bath, and, after the cessation of the reaction and evaporation of the chloroform, treating the residual yellow syrup with concentrated aqueous ammonia, is a yellow syrup which is converted by the Schotten-Baumann method into *β -hippurylaminoethyl hippurate*, $\text{NHBz}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{NHBz}$, colourless leaflets, m. p. 144°.

Dicarbaminoethyl carbonate, $\text{CO}\langle\begin{smallmatrix} \text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O} \\ \text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O} \end{smallmatrix}\rangle\text{CO}$, crystals, m. p. 88—90°, is obtained by the prolonged action of carbonyl chloride on β -aminoethyl alcohol in chloroform solution in the presence of lead carbonate.

β -Aminoethyl alcohol in very dilute solution responds to the iodoform test. By treating an aqueous solution of the amino-alcohol with sodium nitrite and Ehrlich's reagent (2% alcoholic *p*-dimethylaminobenzaldehyde and dilute hydrochloric acid), an intense canary-yellow coloration is produced which is not destroyed by warming or by the addition of aqueous ammonia or potassium hydroxide.

β -Benzoylaminoethyl alcohol, *β -m-aminobenzoylaminoethyl m-aminobenzoate hydrochloride*, and *β -p-aminobenzoylaminoethyl p-aminobenzoate* are not anaesthetics. C. S.

β -Hydroxytrimethylenediglycine. HUGO KRAUSE (*Ber.*, 1918, **51**, 1556—1571. Compare A., 1918, i, 156, 337).— β -Hydroxytrimethylenediglycine has D_{20}^{25} 1.348 by the swimming method. Its solution in formalin or water produces on a pine shaving a greenish-yellow, but not very intense, coloration; the reaction may

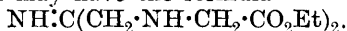
be used as a sensitive method of detecting glycine. The coloration is destroyed by alkali hydroxide or carbonate and by ammonia. Esters of β -hydroxytrimethylenediglycine are obtained by the action of aqueous sodium hydroxide on a solution of the glycine ester hydrochloride in formalin. The *methyl* ester,



a viscous, colourless liquid still containing 10% of formaldehyde, D^{15} 1.18, is obtained in only 19% yield, but the *ethyl* ester is more readily obtained. When pure, it has b. p. 140—150°/16 mm. (partial decomp.), D^{15} 1.150, and a molecular weight in benzene or naphthalene corresponding with its formula. It is comparatively stable towards sodium hydroxide, but is decomposed quantitatively by cold dilute hydrochloric acid, yielding methyl alcohol, formaldehyde, and ethyl glycine hydrochloride.

When the ethyl ester (84% purity) is heated at 16—18 mm., the distillate, apart from formaldehyde and unchanged ester, consists of a pale yellow oil, b. p. 200°/16 mm., which appears to be *ethyl methyleneglycine*, $\text{CH}_2\cdot\text{N}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, or *ethyl ethylenediglycine*, $\text{C}_2\text{H}_4(\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et})_2$, more probably the former.

In the expectation of preparing the amide, ethyl β -hydroxytrimethylenediglycine was heated with alcoholic ammonia at 68—70° for twenty-four hours, but the chief product was a *substance*, $\text{C}_{11}\text{H}_{21}\text{O}_4\text{N}_3$, which may have the formula



The silver salt, $\text{C}_3\text{H}_6\text{O}_3\text{NAg}$, previously described (*loc. cit.*), can also be prepared by dissolving glycine in 30% formaldehyde solution in the cold, neutralising this solution immediately with 4*N*-potassium hydroxide (phenolphthalein as indicator), and adding 20% silver nitrate solution. It is decomposed in aqueous suspension by hydrogen sulphide, yielding formaldehyde and glycine. The acid corresponding with the silver salt is therefore probably *N*-hydroxymethylglycine, $\text{OH}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$.

C. S.

Comparisons and Similarities: Water and Ammonia.

G. CIAMICIAN (*Atti R. Accad. Lincei*, 1918, [v], **27**, ii, 141—146). —Attention is directed to the chemical analogy between OH_2 and NH_3 , between $\cdot\text{OH}$ and $\cdot\text{NH}_2$, and between :O and :NH (compare Angeli, A., 1910, ii, 844, 948; 1915, i, 847). Such analogy is clearly shown in the relation between $\text{C}\text{:O}$ and $\text{C}\text{:NH}$, the ready oxidation of cyanides to cyanates corresponding with that of carbon monoxide to carbon dioxide, and the reduction by zinc of cyanic acid with that of carbon dioxide. These relations are further rendered evident by the following series of equations: $\text{CO}_2 + \text{H}_2\text{O} = \text{CO}(\text{OH})_2$; $\text{CO}_2 + \text{NH}_3 = \text{OH}\cdot\text{CO}\cdot\text{NH}_2$; $\text{O}\text{:C}\text{:NH} + \text{NH}_3 = \text{CO}(\text{NH}_2)_2$; $\text{C}(\text{:NH})_2 + \text{H}_2\text{O} = \text{CO}(\text{NH}_2)_2$; $\text{C}(\text{:NH})_2 + \text{ROH} = \text{OR}\cdot\text{C}(\text{:NH})\cdot\text{NH}_2$; $\text{C}(\text{:NH})_2 + \text{NH}_3 = \text{NH}\cdot\text{C}(\text{NH}_2)_2$. The polymerisation of cyanamide to dicyanodiamide corresponds with the synthesis of guanidine and its derivatives, the two tautomeric forms of cyanamide being regarded as reacting: $\text{C}(\text{:NH})_2 + \text{CN}\cdot\text{NH}_2 = \text{NH}_2\cdot\text{C}(\text{:NH})\cdot\text{NH}\cdot\text{CN}$. Other similar analogies are recorded.

T. H. P.

Formation of Carbamide from Ammonium Carbonate and Related Substances. FR. FICHTER, HEINRICH STEIGER, and THEOPHIL STANISCH (*Verh. Schweiz. Nat. Ges.*, 1916, **28**, ii, 66—103; from *Chem. Zentr.*, 1918, ii, 444—446).—In a previous communication (Fichter, Stutz, and Grieshaber, A., 1913, i, 713), the formation of carbamide by the electrolysis of ammonium carbamate was attributed to the intermediate production of formamide by the action of hydroxylamine on ammonium carbamate; this view can no longer be maintained, since direct experiment shows that ammonium carbamate is not reduced by hydroxylamine. On the other hand, carbon dioxide reacts with hydroxylamine in the same manner as with ammonia, giving, according to conditions, hydroxylamine carbonate or the dihydroxylamine salt of hydroxycarbamic acid, $\text{OH}\cdot\text{NH}\cdot\text{CO}_2\text{H}, 2\text{NH}_2\cdot\text{OH}$. The experiments on the electrolysis of ammonium carbamate solution (*loc. cit.*) have therefore been repeated, the same solution being used as in previous experiments, but every care being taken to keep the anode and cathode solutions separate by enclosing the electrodes in porous pots immersed in a trough, all vessels containing the same solution. The results show that carbamide is produced exclusively at the anode, but no trace of a corresponding reduction product, such as formic acid or formamide, could be detected at the cathode. Under the experimental conditions, Liebig's method of detecting carbamide is unsuitable, but Fosse's method (A., 1914, ii, 756) gives trustworthy results, is not affected by the presence of ammonium salts, and allows the isolation of carbamide by the action of alcoholic hydrogen chloride on the dioxanthylcarbamide.

Attempts have also been made to effect the oxidation of ammonium carbamate to carbamide by purely chemical means; hydrogen peroxide or calcium permanganate gives small but distinctly recognisable quantities of carbamide. Oxidation may also be effected by ozone, either by leading ozonised oxygen into ammonium carbamate solution or over powdered ammonium carbonate, or by mixing ozonised oxygen, ammonia, and carbon dioxide. The yield depends on the concentration of ammonia and the temperature. The chemical and electrochemical oxidations have the transformation of ammonia into ammonium nitrate as a common feature; also, the local increase in temperature caused by the reaction is sufficient to cause a purely thermal transformation of ammonium carbamate into carbamide.

The general explanation of the equilibrium between ammonium carbamate and carbamide is that the former passes into the latter by loss of a molecule of water. This, however, is opposed to the law of mass action; the change is more probably represented by the scheme: $\text{NH}_2\cdot\text{CO}_2\text{NH}_4 + \text{H}_2\text{O} \rightleftharpoons (\text{NH}_4)_2\text{CO}_3 \rightleftharpoons \text{CO}(\text{NH}_2)_2 + 2\text{H}_2\text{O}$. Direct experiment shows that the rate of formation of carbamide is increased by water in the early stages of the reaction, as is required by the above hypothesis. The authors are therefore led to the conclusion that normal ammonium carbonate is the

actual source of carbamide; since, however, the presence of water has an effect disadvantageous to the carbamide in the final equilibrium, $(\text{NH}_4)_2\text{CO}_3 \rightleftharpoons \text{CO}(\text{NH}_2)_2 + 2\text{H}_2\text{O}$, it is advisable to operate with substances containing the components of ammonium carbonate, but having less water, such as ammonium carbamate. At the temperature of the reaction, the small quantity of hygroscopic moisture is sufficient to start the conversion of the carbamate into carbonate, and as soon as the latter commences to be transformed into carbamide, water is liberated in amount sufficient to complete the hydration of the carbamate. In the anhydrous condition, ammonium carbamate is more stable than the carbonate; in the presence of water, however, it becomes unstable, and, above a certain temperature, is incapable of existence. In the region above 135° , there is only the equilibrium between ammonium carbonate and carbamide, in which the latter is favoured by further rise of temperature; below 135° , on the other hand, the complex equilibrium of the first scheme exists. The maximum yield obtained at 135° thus finds a simple explanation. The equilibrium, $(\text{NH}_4)_2\text{CO}_3 \rightleftharpoons \text{CO}(\text{NH}_2)_2 + 2\text{H}_2\text{O}$, has been investigated at 125° , 100° , 78° , and $37\text{--}38^\circ$, and the combined effects of temperature and dilution are explicable from the point of view of the complex equilibrium scheme. Lowering of temperature renders the carbamate and the carbamide more stable; increase in the quantity of water acts in the opposite direction in each case. According to the preponderance of one or the other factors, the following effects may be observed at temperatures below 135° with a constant molecular ratio of carbamate to water: (1) the second portion of the scheme may be so far favoured that the yield of carbamide is increased, since the amount of water suffices to convert a larger proportion of carbamate into carbonate in spite of the actual increased stability of the former; (2) the yield may remain constant, since the increase in stability of the carbamate balances the increased tendency to formation of carbamide; (3) the increased stability of the carbamate is not counterbalanced by the amount of water, and the yield of carbamide sinks. All three possibilities have been experimentally realised. Free ammonia favours the carbamide in the equilibrium, $(\text{NH}_4)_2\text{CO}_3 \rightleftharpoons \text{CO}(\text{NH}_2)_2 + 2\text{H}_2\text{O}$, in the absence of water, but is without influence in presence of the latter.

H. W.

Acetylmethylcarbamide. ROBERT BEHREND and HANS ODENWALD (*Annalen*, 1918, **416**, 228—229).—Fifty-nine grams of acetamide (1 mol.) are dissolved in 88 grams of bromine (0.55 mol.), a 20% solution of potassium hydroxide (56 grams; 1 mol.) is added, the solution is heated on the water-bath until it becomes yellow and is no longer alkaline, and is then cooled, when acetylmethylcarbamide crystallises. Further quantities can be obtained from the mother liquor, the total yield being 75% of the theoretical. With even a slight excess of alkali, the yield falls to zero. C. S.

Substitution in Aromatic Compounds. H. J. PRINS (*Chem. Weekblad*, 1918, **15**, 571—580).—It has been shown in an earlier paper (*ibid.*, 98) that substitution in aromatic compounds begins by addition to a carbon atom of the ring, followed by reaction with the hydrogen atom attached to that carbon atom; the reactivity of the hydrogen atom depends, therefore, in the first place, on the degree of unsaturation of the atom to which it is attached, as is true also in the case of alcohols and amines. Since unsaturation is distributed over the whole nucleus, addition can obviously occur at more than one carbon atom. The analogy with alcohols and amines is shown, not only in the carbon atoms of the nucleus, but in oxygen or nitrogen atoms in side-chains attached to the nucleus, and substitution can be brought about in all these cases by the same catalysts.

Substitution may be not only direct, but indirect also, as in the case of chloroacetanilide; the reaction here is unimolecular, and may be ascribed to a disturbance of the equilibrium between the energy of the atoms (atom-energy) and the energy of combination between the atoms (link-energy). Substitution occurs, then, in the first place at the least saturated carbon atom, but this may not yield the most stable system, and the substituting group may finally take up a different position.

The entry of any substituent X into the benzene ring must cause a change in the relation between atom-energy and link-energy, both in the substituent and in the nucleus. Two cases may arise. In the first, in which the link-energy between X and C₁, the carbon atom to which X becomes attached, is greater than that between C₁ and the hydrogen atom displaced; the atom-energy of C₁ is therefore reduced, and to restore this as far as possible, the link-energy between C₁ and its neighbours, C₂ and C₃, is reduced, with the consequence that the link-energy between C₂ and C₄ and between C₃ and C₅ is increased (C₄ and C₅ being the neighbours of C₂ and C₃ remote from C₁), and that between C₄ and C₆ and C₅ and C₆ is diminished; C₆, therefore, by the diminution of its link-energy, receives an increase of atom-energy and is therefore rendered more reactive. The effect of introducing X, therefore, is to make the para-carbon atom more reactive. In the second case, in which the link-energy between C₁ and the substituent is less than between C₁ and hydrogen, the redistribution of energy causes an increase in the atom energy of C₄ and C₅, that is, of the carbon atoms in the meta-position.

The fact that a substituent which directs a second substituting group to the meta-position also causes a reduction in the velocity of substitution is taken to indicate that the atom-energy of the atoms of the substituted nucleus is less than that of the atoms of the unsubstituted benzene ring itself, and hence it follows that the introduction into the ring of a group which directs to the meta-position causes the transformation of atom-energy into link-energy throughout the ring as a whole.

It is shown that substitution in the benzene ring cannot be explained by the assumption of a conjugated system, as attempted by Böeseken (A., 1912, i, 430) and by Holleman (*Chem. Weekblad*, 1913, 10, 615, 618), without postulating many other conditions.

S. I. L.

Pyrogenic Acetylene Condensations. V. RICHARD MEYER and WILHELM MEYER (*Ber.*, 1918, 51, 1571—1587. Compare A., 1917, i, 313).—In addition to the substances previously identified in the product of the pyrogenic condensation of acetylene, *o*-xylene (identified as *o*-phthalic acid) and indene have been detected and the presence of mesitylene and ψ -cumene confirmed. Durene and isodurene could not be detected. The methylthiophen obtained by the condensation of acetylene, methane, and hydrogen sulphide (*loc. cit.*) is proved to be α -thiotolene, and thionaphthen has been found in the product of the condensation of acetylene and hydrogen sulphide. A complete list is given of all the products obtained by pyrogenic acetylene condensations.

Hydrindene brominated in the cold in the presence of a little iodine yields 4:5:6:7-tetrabromohydrindene, $C_6Br_4 \begin{smallmatrix} <CH_2> \\ <CH_2> \end{smallmatrix} CH_2$, needles, m. p. 200° (which is converted into tetrabromophthalic acid by oxidation), but, brominated in boiling chloroform, yields 1:2:3-tribromohydrindene, feathery crystals, m. p. 134°, which yields phthalic acid by oxidation, and is also obtained by the further bromination of indene dibromide.

About 0.5 c.c. of aniline was obtained when the vapour of 3 litres of benzene mixed with ammonia was passed during twenty-four hours through a tube heated at 550° initially and at 700° finally; aniline could not be detected if the temperature was maintained at 550° throughout. [See also *J. Soc. Chem. Ind.*, 1919, 35A.]

C. S.

The Optically Active neoMethylhydrindamines. JOSEPH WALTER HARRIS (*T.*, 1919, 115, 61—67).

The Fusion of Sodium Hydroxide with Several Phenols and Sulphonic Acids. MAITLAND C. BOSWELL and J. V. DICKSON (*J. Amer. Chem. Soc.*, 1918, 40, 1786—1793).—A number of experiments were carried out in which sodium benzenesulphonate was fused with sodium hydroxide at temperatures of 300—350° in a closed vessel in presence or absence of air, the gaseous contents of the tube being analysed before and after the experiments. It was found that when the fusion was carried out in presence of air, a considerable quantity of hydrogen was formed and a much smaller quantity of methane or other gaseous hydrocarbon. At the same time, some of the oxygen originally present disappeared, the volume ratio of hydrogen formed to oxygen used up being approximately 1:2. When air is excluded from the fusion, however, no hydrogen or methane appears. It was found, working on comparatively large quantities of material, that by

carrying out the fusion in an atmosphere of nitrogen instead of air, the yield of phenol could be increased from 90% to 98% of the theoretical.

In the presence of free oxygen, secondary reactions evidently occur involving the absorption of oxygen, followed by an oxidation involving the elements of water. To determine whether any of the dihydroxy- or trihydroxy-benzenes are formed as secondary products, the fusion of all six of these with sodium hydroxide in presence or absence of air was studied. In the case of five of them, hydrogen was formed in presence, not in absence of air. In the case of hydroxyquinol, much hydrogen is evolved even in absence of air, and also considerable quantities of methane. It is not considered that any of these can be the direct cause of hydrogen formation in the benzenesulphonate fusion.

Sodium hydroxide does not bring about catalytic oxidation of the dihydroxybenzenes, of pyrogallol, of β -naphthalenesulphonic acid, or phenylglycine-*o*-carboxylic acid. With sodium anthraquinone- β -sulphonate, however, oxidation occurs in absence of oxygen, with formation of free hydrogen. E. H. R.

The Miscibility of Phenol and Alkaline Solutions. RENÉ DUBRISAY, TRIPIER, and TOQUET (*Compt. rend.*, 1918, 167, 1036—1038).—The coefficient of reciprocal miscibility of phenol and water steadily increases with the addition of alkali hydroxides to the water. Curves are given for sodium hydroxide at concentrations varying from $N/20$ to $N/3$. The action of the alkaline earth hydroxides is similar, but less marked. On the other hand, acids and salts of the strong acids cause a diminution in the coefficient, and the same holds good for the alkali carbonates.

W. G.

Aromatic Derivatives of Orthosulphurous Acid. M. M. RICHTER (*Annalen*, 1918, 416, 291—304. Compare A., 1917, i, 24).—The attempt to prepare aryl sulphates in the same way as aryl sulphites (*loc. cit.*) by means of sulphuryl chloride and pyridine failed, chlorinated liquid products being obtained. Phenyl sulphate is obtained indirectly by dissolving phenyl sulphite in concentrated sulphuric acid with cooling and pouring the solution into water. The amorphous precipitate obtained separates from formic acid solution in plates with blunted angles, m. p. 288° (decomp.; rapidly heated) or 280 — 282° (decomp.; slowly heated). The substance is regarded as a double salt of diphenyl sulphate (1 mol.) and diphenyl sulphite (2 mols.) having the formula $\text{SO}_3[\text{O}\cdot\text{S}(\text{OPh})_3]_2$, that is, it is a *sulphate of triphenyl-orthosulphurous acid*. It is easily soluble in formic, sulphuric, and phosphoric acids, in methyl sulphate and in alkali hydroxides and carbonates, ammonia and alkali sulphides, dissolves slightly in warm methyl or ethyl alcohol and in boiling water, and is insoluble in all other common solvents. It is converted by alcoholic hydrochloric acid at 70° into the *chloride of triphenyl-orthosulphurous acid*, $\text{S}(\text{OPh})_3\text{Cl}$, long, prismatic needles, m. p. 256° (decomp.), and in dilute potassium hydroxide solution by a solution of pyridine

hydrochloride containing an excess of pyridine into *triphenylorthosulphurous acid*, $\text{OH}\cdot\text{S}(\text{OPh})_3$, an amorphous powder, m. p. 233° . The last substance is amphoteric. Its acidic character is weaker than that of carbonic acid, whilst its basic properties are such that a hot 50% alcoholic solution has an alkaline reaction towards litmus. The three phenyl groups are not eliminated by hydrolysing agents. By treating an alcoholic suspension of the acid with the requisite acid, the *bromide*, $\text{S}(\text{OPh})_3\text{Br}$, needles, m. p. $241\text{--}242^\circ$ (decomp.), *iodide*, short needles, m. p. $194\text{--}195^\circ$ (reddening), *nitrate*, hair-like needles, m. p. $160\text{--}161^\circ$ (decomp.), *acetate*, waxy mass, and *picrate*, yellow mass, are obtained. *Ethyl triphenylorthosulphite*, $\text{OEt}\cdot\text{S}(\text{OPh})_3$, amorphous powder, m. p. 244° (decomp.), is obtained from the chloride and alcoholic sodium ethoxide.

The *sulphate*, $\text{SO}_2[\text{O}\cdot\text{S}(\text{O}\cdot\text{C}_6\text{H}_4\text{Me})_3]_2$, crystals, m. p. 296° (decomp.), prepared from di-*o*-tolyl sulphite, and the corresponding *sulphate*, m. p. 315° (decomp.), prepared from di-*m*-tolyl sulphite, are obtained in the same way as the phenyl analogue; the latter yields *tri-m-tolylorthosulphurous acid*, amorphous powder, m. p. 267° (decomp.), by treatment with pyridine hydrochloride as above.

The colourless, amorphous *sulphate*, m. p. 232° (decomp.), obtained by pouring a solution of dithymyl sulphite in concentrated sulphuric acid into water, is regarded as a mixed anhydride of sulphuric, dithymylorthosulphurous, and trithymylorthosulphurous acids, $(\text{C}_{10}\text{H}_{13}\cdot\text{O})_3\text{S}\cdot\text{O}\cdot\text{SO}_2\cdot\text{O}\cdot\text{S}(\text{O}\cdot\text{C}_{10}\text{H}_{13})_2\cdot\text{OH}$. It is soluble in alcohol, but by treating its solution in aqueous-alcoholic potassium hydroxide with alcoholic sulphuric acid, a *sulphate*, $\text{SO}_2[\text{O}\cdot\text{S}(\text{O}\cdot\text{C}_{10}\text{H}_{13})_3]_2$, amorphous powder, m. p. $280\text{--}281^\circ$ (decomp.), is precipitated, which is insoluble in alcohol. The insoluble sulphate yields *trithymylorthosulphurous acid*, amorphous powder, m. p. $274\text{--}275^\circ$ (decomp.), by the pyridine hydrochloride method, whilst the soluble sulphate, by treatment with alcohol and the requisite acid, yields the *chloride*, $\text{SCl}(\text{O}\cdot\text{C}_{10}\text{H}_{13})_3$, amorphous powder darkening at $295\text{--}300^\circ$ without melting, *bromide*, small crystals, decomp. $330\text{--}340^\circ$, *iodide*, crystals, and *nitrate*, small, rectangular plates blackening at $285\text{--}290^\circ$ without melting.

C. S.

Thiophenol in Synthetic Phenol. G. CAPPELLI (*Gazzetta*, 1918, **48**, ii, 107—113).—The repulsive odour exhibited by some samples of synthetic phenol is sometimes attributed to the presence of thiophen in the benzene used in the manufacture. The author shows that such odour is due to a small proportion of thiophenol, formed from particles of sodium benzenesulphonate which, during the fusion with alkali, escape contact with the latter and undergo deoxidation at the surface of the iron in the manner observed by Stenhouse (*Annalen*, 1866, **140**, 284; 1869, **149**, 42). The phenol may be freed from this impurity by fusing it, adding a little alcohol to keep it liquid, and then adding, per kilo. of phenol, about 50 c.c. (more, if continued formation of precipitate shows it to be neces-

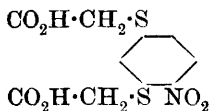
sary) of 10% alcoholic mercuric chloride solution. The excess of mercuric chloride is eliminated by leaving the clear liquid for a couple of days in contact with copper turnings or foil; the mercury deposited on the latter may be recovered by distillation. Fractional distillation of the decanted solution gives: (1) below 179°, water and alcohol, and (2) at 179—183°, pure phenol with its characteristic odour. T. H. P.

Organic Salts of Bivalent Chromium. G. SCAGLIARINI (*Atti R. Accad. Lincei*, 1918, [v], 27, ii, 87—89; *Gazzetta*, 1918, 48, ii, 148—150).—The greyish-green salt obtained by Calcagni (A., 1913, i, 1154) either from chrome alum and sodium salicylate or from chromic hydroxide and salicylic acid, and regarded by him as a chromous compound, is probably a salt of tervalent chromium in which also the phenolic hydroxyl groups take part in the salt-formation. All other chromous salts of organic acids, including those now described by the author, are red.

Chromous salicylate, $C_6H_4 \begin{smallmatrix} \diagup CO \cdot O \\ \diagdown O \end{smallmatrix} Cr, 3H_2O$, prepared by reducing chrome alum solution with zinc and hydrochloric acid and adding sodium salicylate solution free from air, forms small, red crystals, but rapidly oxidises and becomes greenish-grey in the air.

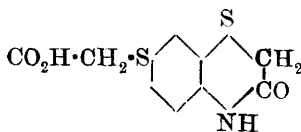
Chromous propionate, $2(C_3H_5O_2)_2Cr, H_2O$, was also prepared and analysed, and the butyrate and valerate prepared. T. H. P.

Nitro-2:4-phenylenedithioglycollic Acid and Some of its Colouring Derivatives. C. FINZI and N. BOTTIGLIERI (*Gazzetta*, 1918, 48, ii, 113—122).—The authors have prepared the nitro-derivative of *m*-phenylenedithioglycollic [*m*-phenylenedithiolacetic] acid, and as this yields on reduction, not an amino-acid, but a ketothiazine derivative, the conclusion is drawn that the nitro-group enters the benzene nucleus in the ortho-position to one of the substituents. The sulphone corresponding with the nitro-compound undergoes ring-closure on reduction still more easily, the resultant compound being quite analogous to Clausz's sulphazone (A., 1912, i, 389), and being hence termed sulphazon-sulphonacetic acid. This acid has been coupled with various diazo-compounds, the derivatives thus obtained being of different colours and serving as substantive dyestuffs for silk.



4-Nitro-m-phenylenedithiolacetic acid (annexed formula), obtained from *m*-phenylenedithiolacetic acid and nitric acid, forms slender, yellow needles, m. p. 174°.

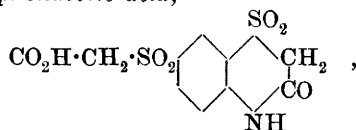
2-Keto-2:3-dihydrothiazine-6-thiolacetic acid (annexed formula), obtained by reducing the previous compound, forms tufts of silky, white needles, m. p. 210°; its sodium salt (+ 3H₂O) was prepared and analysed.



4-Nitro-m-phenylenedisulphonacetic acid, $NO_2 \cdot C_6H_3(SO_2 \cdot CH_2 \cdot CO_2H)_2$, prepared by the action of hydrogen per-

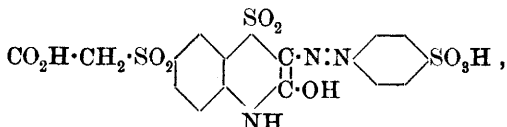
oxide on the nitro-acid, forms long, white needles, m. p. 199° (decomp.). On reduction with tin and hydrochloric acid, it yields

Sulphazon-6-sulphonacetic acid,



which forms white, mammillary masses of slender needles, m. p. 219° (decomp.).

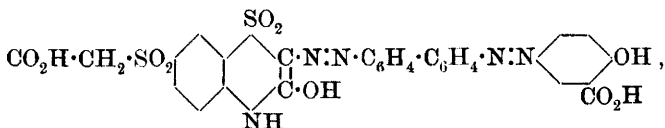
p-Sulphobenzeneazosulphazon-6-sulphonacetic acid,



obtained by condensing the preceding acid with diazobenzene-sulphonic acid, forms small needles of the colour of chromic anhydride. At 40—50° in aqueous solution, it is fixed directly on silk, giving a brilliant orange-yellow colour stable against soap and light; wool fixes it with more difficulty, but assumes a stable, yellow coloration. *4-Sulphonaphthaleneazosulphazonacetic acid*,



dyes silk an old-gold yellow stable against soap and light. *Salicylic-acid-p-azodiphenyl-p'-azosulphazonsulphonacetic acid*,

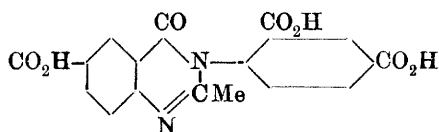


forms a brownish-black colouring matter almost insoluble in water, and directly colours silk yellow with an olive-green tinge.

T. H. P.

4-Aminoisophthalic Acid and its Derivatives. RUDOLF WEGSCHEIDER, HANS MALLE, ALFRED EHRLICH, and ROBERT SKUTEZKY (*Monatsh.*, 1918, **39**, 375—417).—4-Acetylaminoisophthalic acid is conveniently prepared by oxidising 4-aceto-m-xylidide with a boiling aqueous solution of calcium permanganate; when rapidly heated, it becomes yellow at about 270°, melts at 295—296° (corr.; decomp.), immediately resolidifies, and then remains unchanged up to 350°; when slowly heated, decomposition frequently occurs without visible liquefaction. (The calcium salt

[+ 3H₂O] is described.) During the heating, one molecule of acid loses its acetyl group, and the residue reacts as an amine with a second molecule of acid, yielding thereby 4-*keto*-3-*phenyl*-2-*methyl*-3:4-*dihydroquinazoline*-6 : 2' : 4'-*tricarboxylic acid* (annexed



formula), m. p. 416° (corr.). [*Ethyl* ester, m. p. 332° (corr.) after sintering at 330°.]

The esters of 4-acetyl-aminoisophthalic acid were prepared by acetylation of the corresponding esters of the amino-acid: *methyl 4-acetyl-aminoisophthalate* has m. p. 125—126°; 1-*methyl 3-hydrogen 4-acetyl-aminoisophthalate* melts at 218—219°; the corresponding normal and acid ethyl esters have m. p.'s 109—110° and 193·5—194·5° respectively. Attempts to esterify the acetyl-amino-acid by methyl alcohol and mineral acids led, as in the case of acetylaminoterephthalic acid (Wegscheider and Faltis, A., 1912, i, 463) to the deacetylation of the acid.

4-Aminoisophthalic acid is most conveniently prepared from its acetyl derivative by esterifying the latter with methyl alcohol and mineral acid, and subsequent hydrolysis of the purified amino-ester so formed; it has m. p. 336—337° (corr.; decomp.). The *dimethyl* and *diethyl* esters have m. p.'s 131·5° and 79—80° respectively, whilst 1-*methyl 3-hydrogen 4-aminoisophthalate* and the corresponding *ethyl* ester melt at 224—225° (decomp.) and 216·5—218°. The acid behaves contrary to the usual rule, since it yields the same ester by treatment with mineral acid and methyl alcohol and by half-hydrolysis of the normal ester.

The methylation of the amino- and acetyl-amino-acids and their esters has been studied under varying conditions. 4-*Dimethyl-aminoisophthalic acid* is most conveniently prepared by treatment of the corresponding dimethyl ester with methyl sulphate at 100° and hydrolysis of the *ester* (m. p. 70°) with alcoholic potassium hydroxide; its m. p. depends greatly on the mode of heating. The silver *salt* is described. Methylation of the free acid is very incomplete either by the action of methyl sulphate on the dry potassium salt in the presence of potassium hydroxide solution or in the presence of water and barium carbonate. The use of methyl iodide and potassium hydroxide does not lead to better results. 4-Acetyl-aminoisophthalic acid is methylated with still greater difficulty, yielding small amounts of dimethyl-aminoisophthalic acid. Methyl sulphate does not act on dimethyl 4-acetyl-aminoisophthalate below 115°; at 120—124°, however, *trimethyl 4-keto-3-phenyl-2-methyl-3 : 4-dihydroquinazoline*-6 : 2' : 4'-*tricarboxylate*, m. p. 205·5°, is produced.

4-Acetylmethylaminoisophthalic acid is prepared by the action of methyl iodide on the sodium or, preferably, the potassium salt of dimethyl 4-acetyl-aminoisophthalate and subsequent hydrolysis with alcoholic potassium hydroxide solution; it forms colourless

needles, the m. p. of which depends on the mode of heating. 4-Methylaminoisophthalic acid has m. p. 297·5—298·5° (corr.) after decomposition at 296° when placed in a bath preheated to 293°; the corresponding *dimethyl* ester melts at 115°. 1-Methyl 3-hydrogen 4-methylaminoisophthalate, m. p. 238—239° (decomp.), is obtained by the partial esterification of 4-methylaminoisophthalic acid with methyl alcohol and hydrogen chloride. H. W.

Colour and Chemical Constitution. III. Derivatives of the Unknown *op*-Phenolphthalein. JAMES MOIR (*Trans. Roy. Soc. S. Africa*, 1918, 7, 123—127. Compare A., 1917, ii, 349, 557).—The preparation and absorption spectra of a number of phthalein derivatives containing one hydroxyl group in the *ortho*- and a second in the *para*-position to the central carbon atom are described. Thus *phenol-p-cresolphthalein* is obtained by heating a mixture of *p*-cresol and *p*-hydroxybenzoylbenzoic acid in the presence of zinc chloride. The following substances are prepared in a similar manner: *op-phenolphthalein-m-carboxylic acid* and its *methyl ether*, *hydroxydiphenylphthalidecarboxylic acid*, *m-amino-op-phenolphthalein*, the corresponding *m-methylamino*-derivatives and its *ω-carboxylic acid*, *m-phenyl-op-phenolphthalein*, and *m-nitro-op-phenolphthalein*. Attempts to prepare *op-phenolphthalein* by reduction of *m-iodo-op-phenolphthalein* did not yield the desired result, and further work in this direction was abandoned, since it was discovered that *p*-hydroxybenzoylbenzoic acid yields a phthalein-like substance when heated at above 200°, or at a lower temperature in the presence of concentrated sulphuric acid; this substance, which resembles phenolphthalein very closely, can also be obtained by heating phenolphthaleinoxime with a small quantity of sulphuric acid at above 200°, and it therefore appears probable that the so-called oxime is in reality the *p*-hydroxyanilide of *p*-hydroxybenzoylbenzoic acid.

It is possible to find a particular strength of alkali in which any phthalein gives a colourless solution in the cold, but which becomes coloured on heating to near the boiling point, and again fades on cooling and keeping. For ordinary phenolphthalein, the concentration of alkali is slightly above normal; tetraiodo-phenolphthalein requires a much weaker alkali, whilst α -naphtholphthalein requires about 2*N*-alkali.

Phenolphthalein-*o*-carboxylic acid is coloured faintly pink by ammonia and deep violet-pink by alkali hydroxide; as an indicator, it resembles thymolphthalein, but has a more favourable colour. The corresponding dicarboxylic acid is useful in proving the presence of definite caustic alkalinity at about *N*/100.

H. W.

Constitution of the Hydrazone of Benzaldehyde. J. SUREDA BLANES (*Anal. Fis. Quím.*, 1918, 16, 707—718).—The author summarises the evidence for and against the cyclical formula of Curtius for the aliphatic diazo-compounds, $RR\cdot C < \begin{smallmatrix} N \\ N \end{smallmatrix}$, as com-

pared with the lineal formula, $RR \cdot C:N:N$, suggested by Angeli and later by Thiele.

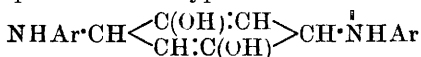
The easy oxidation of hydrazones to diazo-compounds suggests the investigation of the constitution of the former substances. The hydrazone chosen for preliminary examination is that of benzaldehyde, which on oxidation gives phenyldiazomethane. The alternative structures which may be assigned to benzaldehydehydrazone are: $CHPh \begin{smallmatrix} \text{NH} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix}$ and $CHPh:N \cdot NH_2$.

The following reactions establish the latter formula:

- (1) Benzaldehydehydrazone and phenylcarbimide,
 $CHPh:N \cdot NH_2 + CONPh = NPh \cdot CO \cdot NH \cdot N:CHPh$.
- (2) Benzaldehydehydrazone and phenylthiocarbimide,
 $CHPh:N \cdot NH_2 + SCNPh = NPh \cdot CS \cdot NH \cdot N:CHPh$.
- (3) Benzaldehydehydrazone and diphenylketen,
 $CHPh:N \cdot NH_2 + CPh_2:CO = CHPh_2 \cdot CO \cdot NH \cdot N:CHPh$.

The product of the last reaction forms white crystals insoluble in alcohol, ether, or benzene, slightly soluble in light petroleum and glacial acetic acid, m. p. 196° . These reactions are incompatible with the cyclical formula for benzaldehydehydrazone, and therefore the lineal formula must be assumed. W. S. M.

Anilinoquinones. HERMANN SUIDA and WILHELM SUIDA (*Annalen*, 1918, **416**, 113—163).—The generally accepted view that anilinoquinones are always formed by the transformation of an additive compound of the type



into $NHAr \cdot C \begin{smallmatrix} \text{CO:CH} \\ \diagdown \quad \diagup \\ \text{CH:CO} \end{smallmatrix} > C \cdot NHAr$, with the removal of four atoms of hydrogen, which reduce two further molecules of the quinone, is found not to hold. In some cases, the reaction recognisably passes through the monoanilide. In the case of the simplest and most reactive components, monoanilides are smoothly formed in accordance with the equation $2C_6H_4O_2 + NH_2Ar = C_6H_3O_2 \cdot NHAr + C_6H_4(OH)_2$. The capacity of the group $\cdot CO \cdot CH:CH \cdot CO \cdot$ to form anilino-compounds must be connected in some way with the structure of the benzene nucleus, because maleic and fumaric esters and the *cis*- and *trans*-modifications of dibenzoylethylene, in which this group occurs, do not react in this way with aromatic amines.

Under the conditions of the authors' experiments, the following generalisations have been made. *p*-Benzoquinone in aqueous, faintly acetic acid solution yields with all pronouncedly basic primary and secondary aromatic amines anilinoquinones, predominantly and even sometimes exclusively monoanilinoquinones. The intensity of the reaction diminishes as the basic character of the amine is weakened by the entrance of acidic substituents. Thus the strongest bases (aniline and its homologues, diamines, etc.) yield mono- and di-anilides simultaneously, the weaker bases (secondary amines, nitroanilines, etc.) yield only monoanilides,

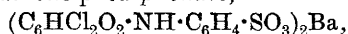
whilst the weakest bases do not react in aqueous solution. Toluquinone yields only monoanilides, and *s*-xyloquinone does not react.

In alcoholic solution, *p*-benzoquinone forms only dianilides; monoanilides are present in the mother liquor only when the basic component contains acidic substituents. Tolu- and naphthaquinones yield only monoanilides, and *s*-xyloquinone none.

The reactions also proceed in glacial acetic acid solution. Therefore by a suitable selection of the solvent and of the temperature it is possible to make a quinone react once or twice with an amine, or a monoanilinoquinone to react with a different base, producing a mixed dianilinoquinone.

The following new derivatives of *p*-benzoquinone have been prepared: 5-anilino-2-*α*-naphthylamino-, $C_{22}H_{16}O_2N_2$, yellowish-brown powder, m. p. 278—280°; 2-*p*-chloroanilino-, sepia crystals, decomp. about 115°; 2:5-di-*p*-chloroanilino-, pale brown crystals; 2-*o*-toluidino-, dark violet-brown crystals, m. p. 100—104°; 2:5-di-*o*-toluidino-, rust-red needles, m. p. 250—252°; 2-*m*-toluidino-, dark violet-brown crystals, m. p. 90—100° (decomp.); 2:5-di-*m*-toluidino-, crimson-red needles, m. p. 256—257°; 2-*p*-toluidino-, aggregates of violet-black needles, m. p. 134—137° (bath at 134°); 2:5-di-*p*-toluidino-, crystals, m. p. 318°; 2-*p*-acetylaminooanilino-, dark crystals; 2-*as-m*-xylidino-, reddish-brown crystals, m. p. 102°; 2:5-di-*as-m*-xylidino-, pale brown crystals, m. p. 297—300°; 2-*ψ*-cumidino-, brick-red crystals, m. p. 90—106°; 2:5-di-*ψ*-cumidino-, pale red crystals, m. p. 301—303°; 2-*o*-anisidino-, brownish-violet leaflets with metallic lustre, m. p. 114° (not sharp).

With the object of preparing monoanilides soluble in water, the aminobenzenesulphonic acids have been utilised. These do not react satisfactorily with *p*-benzoquinone, but give good results with the less reactive 2:6-dichloro-*p*-benzoquinone. By adding to a hot alcoholic solution of this a hot aqueous solution of sulphanilic acid (1 mol.), and subsequently an aqueous solution of sodium acetate (1 mol.), and then barium chloride, barium 2:6-dichloro-5-anilino-*p*-benzoquinone-*p'*-sulphonate,



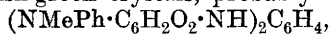
copper-red leaflets, is obtained, the mother liquor containing 2:6-dichloroquinol. If the temperature is about 60° at the beginning and about 30° at the end of the experiment, the product is mainly the barium hydrogen salt. An aqueous solution of the barium salt at 100° rapidly acquires chlorine ions and deposits a blackish-brown powder, which appears to be the barium salt of 2-chloro-5-*p*-sulphoanilino-6-hydroxy-*p*-benzoquinone. By adding sulphanilic acid to a hot aqueous solution of the first-mentioned barium salt, the barium hydrogen salt of 6-chloro-2:5-dianilino-*p*-benzoquinone-*p'*-disulphonic acid is obtained as a brownish-black powder.

2-Methylanilino-*p*-benzoquinone, $C_6H_3O_2 \cdot NMePh$, prepared by adding a cold 50% acetic acid solution of methylaniline (1 mol.) to an aqueous solution of *p*-benzoquinone (2 mols.), forms dark red

needles, m. p. 125—130°. 2:5-Dimethylanilino-*p*-benzoquinone, leaflets, m. p. 205°, is obtained from its components in alcoholic solution.

2-Methylanilino-*p*-benzoquinone, like all other monoanilinoquinones of the same type, yields mixed dianilinoquinones by trituration with an aromatic base or by warming with it in alcoholic solution. The following 2-methylanilino-*p*-benzoquinones of this kind have been prepared: 5-anilino-, $\text{NMePh}\cdot\text{C}_6\text{H}_2\text{O}_2\cdot\text{NHPh}$, orange-red crystals; 5-*p*-carboxyanilino-, dark red leaflets; 5-*m*-carboxyanilino-, brownish-red crystals; 5-*m*-chloroanilino-, garnet-red needles; 5-*o*-hydroxyanilino-, brown leaflets; 5-*m*-hydroxyanilino-, brownish-yellow, metallic crystals; 5-*p*-bromoanilino-, red crystals; 5-*p*-sulphoanilino-, prepared in the presence of sodium carbonate and 3% hydrogen peroxide, and isolated as the sodium salt; 5- α -naphthylamino-, dark brown crystals; 5- β -naphthylamino-, dark violet-brown crystals; 5-*p*-benzeneazoanilino-, violet-brown crystals.

2-Methylanilino-*p*-benzoquinone (2 mols.) and *p*-phenylenediamine (1 mol.) react in boiling alcohol to form a substance, $\text{C}_{32}\text{H}_{26}\text{O}_4\text{N}_4$, brownish-green crystals, probably

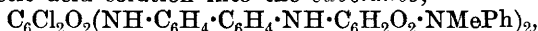


whilst in the ratio of 4:1, in alcohol, glacial acetic acid or nitrobenzene, or by moistening the mixture of the two components with a little solvent and warming on the water-bath, a dark green, crystalline substance, $[(\text{NMePh}\cdot\text{C}_6\text{H}_2\text{O}_2)_2\text{N}]_2\text{C}_6\text{H}_4$, is obtained, m. p. 250—260°.

2-Methylanilino-*p*-benzoquinone and benzidine react in warm alcohol to form the compound,

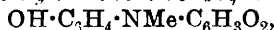


brown needles, m. p. 215—218°, which is converted by chloranil in glacial acetic acid solution into the substance,



crystals. 2-Methyl-*p*-toluidino-*p*-benzoquinone and *p*-phenylenediamine in hot alcoholic solution yield a dark green substance, probably $(\text{C}_7\text{H}_7\cdot\text{NMe}\cdot\text{C}_6\text{H}_2\text{O}_2\cdot\text{NH})_2\text{C}_6\text{H}_4$.

2-Ethylanilino-*p*-benzoquinone forms dark needles, m. p. 85° with previous sintering. 2-Benzylanilino-*p*-benzoquinone forms almost black needles, m. p. 60—70°, whilst 2:5-dibenzylanilino-*p*-benzoquinone, $\text{C}_6\text{H}_2\text{O}_2(\text{NPh}\cdot\text{CH}_2\text{Ph})_2$, crystallises in blood-red needles, m. p. 155—156°. 2-Methyl-*p*-toluidino-*p*-benzoquinone forms reddish-yellow needles, m. p. 127°, and 2:5-dimethyl-*p*-toluidino-*p*-benzoquinone, yellowish-brown, rhombic plates, m. p. 206°. 2-*o*-Hydroxymethylanilino-*p*-benzoquinone,

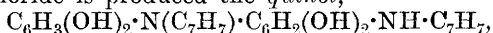


and 2:5-di-*o*-hydroxymethylanilino-*p*-benzoquinone are described.

A table is given of the colorations of the anilinoquinones in concentrated sulphuric acid. C. S.

Polymerisation Phenomena in the Simple Monoanilino-benzoquinones. HERMANN SUIDA (*Annalen*, 1918, 416, 164—181. Compare preceding abstract).—The monoanilinoquin-

ones derived from primary bases are only stable in the pure dry state; they polymerise in solution. Dianilinoquinones, and also monoanilinoquinones derived from secondary bases, show no tendency to polymerise. The polymerisation is probably represented thus: $2\text{C}_6\text{H}_3\text{O}_2\cdot\text{NHA}r \longrightarrow \text{C}_6\text{H}_3\text{O}_2\cdot\text{NA}r\cdot\text{C}_6\text{H}_2(\text{OH})_2\cdot\text{NHA}r$; the dimeric meriquinonoid form produced can undergo further polymerisation. The polymerisation is brought about by heating the monoanilinoquinone at its m. p., by heating with water or dilute acetic acid, by prolonged boiling with alcohol, or by exposing its cold alcoholic solution to intense light. Thus 2-*p*-toluidino-*p*-benzoquinone yields the *dimeride*, $(\text{C}_{13}\text{H}_{11}\text{O}_2\text{N})_2$, m. p. 265—267° (in carbon dioxide), from which by reduction with alcoholic stannous chloride is produced the *quinol*,



pale yellow crystals, m. p. 236—237° (in carbon dioxide). Dimeric *p*-toluidino-*p*-benzoquinone, $\text{C}_6\text{H}_3\text{O}_2\cdot\text{N}(\text{C}_7\text{H}_7)\cdot\text{C}_6\text{H}_2\text{O}_2\cdot\text{NH}\cdot\text{C}_7\text{H}_7$, produced by auto-oxidation by boiling the dimeric meriquinone in glacial acetic acid or nitrobenzene, forms violet-black crystals with green lustre, which remain unchanged at 400°; the oxidation is also effected by ferric chloride in dilute alcoholic solution.

C. S.

Anilinoquinones from Benzoquinone and the Nitroanilines. GUIDO MEYER and HERMANN SUIDA (*Annalen*, 1918, **416**, 181—188).—The nitroanilines do not react as easily as aniline with benzoquinone. In cold aqueous solution, a reaction between the nitroanilines and *p*-benzoquinone is only observed when the nitroaniline is used in the form of its hydrochloride in the presence of an excess of hydrochloric acid; in all three cases, reddish-brown, crystalline additive compounds separate after some hours, but if kept in contact with the mother liquor for several weeks change into the mononitroanilino-*p*-benzoquinones. The latter are obtained immediately from the nitroanilines and *p*-benzoquinone in boiling aqueous solution. 2-*m*-Nitroanilino-*p*-benzoquinone and the *p*-nitro-compound are dark brown and do not crystallise well. The *o*-nitro-compound is less readily obtained. All three compounds have indefinite m. p.'s between 290° and 300°, and develop with sulphuric acid a reddish-violet coloration, which turns blue on warming.

In cold alcoholic solution, a reaction occurs only between *m*-nitroaniline and *p*-benzoquinone, whereby the additive compound is formed. In hot alcoholic or, better, hot glacial acetic acid solution, the 2:5-dinitroanilino-*p*-benzoquinones, decomp. 310—360°, are obtained.

The nitroanilino- and dinitroanilino-*p*-benzoquinones are not attacked by mild reducing agents. Tin and hydrochloric acid convert the latter into phenylenediamines and aminoanilinoquinols, which could not be isolated. *p*-Nitroanilinobenzoquinone was reduced by tin and hydrochloric acid to a base, which was isolated as the *sulphate*, $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2\cdot 2\text{H}_2\text{SO}_4$, prismatic needles; the base itself could not be isolated.

C. S.

Action of the Isomeric Chloromethylanilines on Benzo- and Tolu-quinones. HEINRICH TEUSCHER (*Annalen*, 1918, **416**, 189—202. Compare Suida and Suida, this vol., i, 79).—The chloromethylanilines in aqueous, faintly acetic acid solution yield exclusively monoanilinoquinones with *p*-benzo- and tolu-quinones; as usual, a second molecule of the quinone is reduced to the quinol. Additive products could not be isolated, although they are undoubtedly formed. In alcoholic solution, *p*-benzoquinone yields dianilinoquinones, whilst toluquinone yields only the monoanilinoquinone; here again evidence (colour change) has been obtained of the intermediate formation of additive compounds. Toluquinone, being a weaker oxidising agent than *p*-benzoquinone, reacts more slowly with the aromatic bases. Of these, *o*-chloromethylaniline reacts most slowly and the *p*-compound most rapidly.

2-*p*-Chloromethylanilino-*p*-benzoquinone, $C_6H_3O_2 \cdot NMe \cdot C_6H_4Cl$, is a dark red, crystalline powder, m. p. 145° , the *m*-chloro-compound a reddish-brown powder, m. p. 127° , sintering at 120° , and the *o*-chloro-compound crystallises in pale red needles, m. p. 133° (decomp.), sintering at 60° . 4-*p*-Chloromethylanilino-toluquinone forms a dark red, crystalline powder with metallic lustre, m. p. 156° (from aqueous solution), and dark red needles, m. p. 184° (decomp.) (from alcoholic solution), and the *o*-chloro-compound red leaflets with metallic lustre, m. p. 146° (decomp.).

2:5-Di-*p*-chloromethylanilino-*p*-benzoquinone forms deep bronze leaflets with metallic lustre, m. p. 223° , the *m*-chloro-compound, deep yellow leaflets, m. p. 198° , and the *o*-chloro-compound, reddish-bronze leaflets with metallic lustre, m. p. 258° .

2:5-Di-2':4'-dichloromethylanilino-*p*-benzoquinone, which requires the presence of hydrogen peroxide for its quick preparation, forms brick-red leaflets, m. p. 240° . C. S.

Citronellol. H. J. PRINS (*Chem. Weekblad*, 1918, **15**, 1378—1380).—Distillation of citronellol yields two fractions, one with b. p. 217 — 219° and the other with b. p. 219 — 221° . The liquids probably contain isomerides, but these cannot be separated by fractionation.

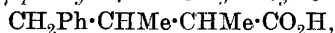
When free from geraniol and other substances, but containing these isomerides, citronellol of maximum purity should have D_{10}^{20} 0.867 — 0.869 , and its index of refraction should be n_D^{20} 1.4586 — 1.4589 . A. J. W.

Constituents of Oil of Cassia. II. FRANCIS D. DODGE (*J. Ind. Eng. Chem.*, 1918, **10**, 1005—1006. Compare A., 1916, i, 155).—Oil of cassia was found to contain cinnamaldehyde (75 to 90%), cinnamyl acetate, phenylpropyl acetate (?), *o*-methoxycinnamaldehyde, salicylaldehyde (0.1 to 0.2%), coumarin, benzoic acid, salicylic acid, an unidentified liquid acid, benzaldehyde, and *o*-methoxybenzaldehyde. [See, further, *J. Soc. Chem. Ind.*, 1919.] W. P. S.

Constitution of Substances from Guaiacum Resin.

G. SCHROETER, L. LICHTENSTADT, and D. IRINEU (*Ber.*, 1918, **51**, 1587—1613).—The milk test with extract of guaiacum resin is not entirely satisfactory, since it depends on the quality of the extract. Before examining the chemistry of the blue compound, it is necessary to determine the structure of the substance (or substances) in the resin which produces it.

The two substances of unknown constitution obtained by the dry distillation of guaiacum resin are guaiene and pyroguaiacin. The latter is known to be a hydroxymethoxy-derivative of the former (Herzig and Schiff, *A.*, 1897, **i**, 254; 1898, **i**, 327, 530). Guaiene is now proved to be 2:3-dimethylnaphthalene by synthesis. *β*-Phenylisopropyl bromide, $\text{CH}_2\text{Ph}\cdot\text{CHMeBr}$, b. p. 107—109°/16 mm., $D^{16.4}_{20}$ 1.2908, obtained from the alcohol and hydrobromic acid (saturated at 0°) at 100°, reacts with ethyl malonate and alcoholic sodium ethoxide on the water-bath to form *ethyl β-phenylisopropylmalonate*, $\text{CH}_2\text{Ph}\cdot\text{CHMe}\cdot\text{CH}(\text{CO}_2\text{Et})_2$, b. p. 182—183°/14 mm., $D^{16.4}_{20}$ 1.0673. This is converted in the usual manner into *ethyl β-phenylisopropylmethylmalonate*, b. p. 188°/16 mm., $D^{18.4}_{20}$ 1.0505, which yields the *acid*, $\text{C}_{13}\text{H}_{16}\text{O}_4$, colourless crystals, m. p. 158—160° (decomp.), by hydrolysis. The acid, heated at 170—190°, yields *γ-phenyl-αβ-dimethylbutyric acid*,



b. p. 179—180.5°/13 mm., the *acid chloride* of which, b. p. 136—143°/13 mm., is converted in light petroleum (b. p. 60—70°) by aluminium chloride into 1-*keto*-2:3-dimethyl-1:2:3:4-tetrahydronaphthalene, b. p. 148—150°/17 mm., m. p. -1°, D^{21}_{20} 1.019. This is reduced by sodium and alcohol to 2:3-dimethyltetrahydronaphthol, m. p. 110—114°, b. p. 148—152°/18 mm., which loses water at above 200° and yields 2:3-dimethyl-Δ¹-dihydronaphthalene, b. p. 120—140°/16 mm., the *dibromide* of which is converted by boiling methyl-alcoholic potassium hydroxide into 2:3-dimethylnaphthalene, m. p. 104—104.5° (picrate, m. p. 123—124°), which is identical with guaiene.

Pyroguaiacin is converted by boiling alcoholic potassium hydroxide and methyl sulphate into *pyroguaiacin methyl ether*, $\text{C}_{12}\text{H}_{10}(\text{OMe})_2$, leaflets, m. p. 149—150°, the oxidation of which by sodium dichromate and glacial acetic acid at 95—115° yields *pyroguaiacinquinone methyl ether*, $\text{C}_{14}\text{H}_{14}\text{O}_4$, yellow needles, m. p. 241—242°. For reasons given below, pyroguaiacin is almost certainly 6-hydroxy-7-methoxy-2:3-dimethylnaphthalene.

Guaiaretic acid, the extraction of which from guaiacum resin by ether is described in detail, has the formula $\text{C}_{20}\text{H}_{24}\text{O}_4$ (Herzig and Schiff, *loc. cit.*, give $\text{C}_{20}\text{H}_{26}\text{O}_4$), and is now found to be optically active, $[\alpha]_D -94^\circ$ in alcohol, and unsaturated. It is converted by methyl sulphate and hot aqueous-alcoholic potassium hydroxide into a *methyl ether*, $\text{C}_{18}\text{H}_{18}(\text{OMe})_2$, colourless needles, m. p. 94—95°, $[\alpha]_D -92^\circ$ in alcohol, which is reduced by sodium and boiling alcohol or in solution in tetrahydronaphthalene at 180° by hydrogen and a nickel catalyst under a pressure of 40—50 kilog.

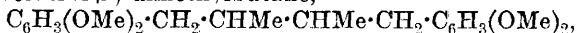
to *hydroguaiaretic acid methyl ether*, $C_{18}H_{18}(OMe)_4$; in both cases a mixture of the *i*-acid, crystals, m. p. 100—101°, and the *l*-acid, flat prisms, m. p. 86—87°, $[\alpha]_D -27^\circ$ in alcohol, is obtained.

Herzig and Schiff's *norguaiaretic acid* (*loc. cit.*), obtained in poor yield from guaiaretic acid and boiling hydriodic acid, is obtained in much better yield from hydroguaiaretic acid methyl ether, and is reconverted into this by methylation; it is therefore *norhydroguaiaretic acid*.

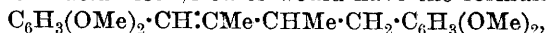
i-Dibromohydroguaiaretic acid methyl ether, $C_{18}H_{16}Br_2(OMe)_4$, colourless needles, m. p. 130·5—131·5°, is obtained by the bromination of *i*-hydroguaiaretic acid methyl ether or guaiaretic acid methyl ether in glacial acetic acid, dehydroguaiaretic acid methyl ether (below) being also formed in the latter case. *l*-Dibromohydroguaiaretic acid methyl ether, colourless crystals, m. p. 121—122°, $[\alpha]_D -42^\circ$ in alcohol, is obtained by brominating *l*-hydroguaiaretic acid methyl ether.

i-Dinitrohydroguaiaretic acid methyl ether, $C_{18}H_{16}(NO_2)_2(OMe)_4$, yellow crystals, m. p. 150—151°, obtained by adding nitric acid, D 1·4, to *i*-hydroguaiaretic acid methyl ether or guaiaretic acid methyl ether in glacial acetic acid solution, is smoothly reduced in tetrahydronaphthalene solution by hydrogen and nickel to *i*-diaminohydroguaiaretic acid methyl ether, faintly violet needles, m. p. 124—125°; attempts to resolve this base by means of *d*-tartaric acid were unsuccessful. *l*-Dinitrohydroguaiaretic acid methyl ether, yellow crystals, m. p. 122—123°, $[\alpha]_D -49·5^\circ$ in glacial acetic acid, is obtained by the nitration of *l*-hydroguaiaretic acid methyl ether.

The reduction of *l*-guaiaretic acid and of its methyl ether yields a mixture of optically active and inactive hydro-derivatives, and therefore possibly racemisation has occurred. Since it is shown, however, that the hydro-derivatives racemise with great difficulty, an alternative explanation of the formation of the inactive modification is that a second carbon atom is rendered asymmetric by the reduction, the inactive hydro-derivative being internally compensated. In favour of the symmetric structure thus postulated is the formation of the probably symmetrically substituted dibromo- and dinitro-derivatives and the failure to resolve the diamino-derivative. Hydroguaiaretic acid methyl ether would therefore be $\alpha\beta$ -diveratryl- $\beta\gamma$ -dimethylbutane,



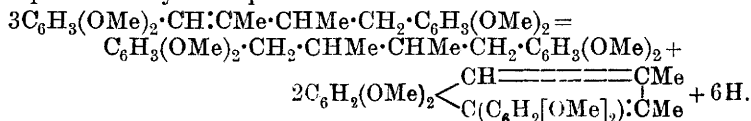
and guaiaretic acid methyl ether would have the formula



the positions of the two methyl groups being determined by the fact that guaiaretic acid can be converted through pyroguaiacin into guaiane (2:3-dimethylnaphthalene).

An extraordinary transformation of guaiaretic acid methyl ether is its *reduction* to hydroguaiaretic acid methyl ether by potassium permanganate in acetone-glacial acetic acid solution, veratric acid also being formed. The explanation is found in the action of Hübl's iodine solution on guaiaretic acid methyl ether (1 mol.),

whereby a mixture of *i*-hydroguaiaretic acid methyl ether and *dehydroguaiaretic acid methyl ether*, $C_{22}H_{24}O_4$, colourless crystals, m. p. 178·5—179°, optically inactive, is obtained in the proportion of 1:2 by the consumption of 1 mol. of iodine. This change is represented by the equation



It is probable, therefore, that in the preceding reaction with potassium permanganate, a portion of the guaiaretic acid methyl ether undergoes ring closure to a naphthalene derivative (which is then oxidised, yielding veratric acid and other products), the hydrogen produced reducing another portion to hydroguaiaretic acid methyl ether, which is stable towards permanganate.

By treatment with 2*N*-sodium hydroxide and methyl sulphate, guaiaconic acid yields a *methyl ether*, an amorphous, yellow powder, m. p. 94—102°, softening at 82°, which, unlike guaiaconic acid, does not develop a blue colour with lead peroxide. By oxidation with potassium permanganate in acetone-glacial acetic acid solution, the ether yields a comparatively large amount of veratric acid and other products, which were not identified.

Believing at first that guaiene was 1:2-dimethylnaphthalene, the authors synthesised this substance as follows. By treatment of their sodio-derivatives with methyl iodide in warm benzene, the *β*-phenylethylmalonic esters yield, respectively, *methyl β-phenylethylmethylmalonate*, b. p. 178—180°/18 mm., and the *ethyl ester*, b. p. 182—184°/12 mm., from which *β-phenylethylmethylmalonic acid*, colourless crystals, m. p. 150° (decomp.), is obtained. At 150—180°, the acid is converted into *γ-phenyl-α-methylbutyric acid*, b. p. 167°/11 mm., the acid *chloride* of which, b. p. 125°/12 mm., is converted in light petroleum solution by aluminium chloride into 1-*keto-2-methyl-1:2:3:4-tetrahydronaphthalene*, b. p. 127—131°/12 mm. This is converted by ethereal magnesium methyl iodide into 1-*hydroxy-1:2-dimethyl-1:2:3:4-tetrahydronaphthalene*, b. p. 135—140°/15 mm., m. p. 64—66°, which at 160—180° yields 1:2-*dimethyl-Δ¹-dihydronaphthalene*, b. p. 250—251°/atm. or 114—116°/15 mm., D_{17}^{20} 0·9885, n_D^{20} 1·5763. The *dibromide* of the latter, a pale yellow oil, is converted by boiling methyl-alcoholic potassium hydroxide into 2-*methyl-1-methylene-Δ²-dihydronaphthalene*, b. p. 157°/15 mm., which yields 1:2-*dimethylnaphthalene*, b. p. 139—140°/15 mm. (*micrate* orange-red crystals, m. p. 129·5—130·5°), by boiling with glacial acetic acid containing hydrogen chloride.

C. S.

Classification of Organic Colouring Matters. M. DOMINIKIEWICZ (*Chem. Zeit.*, 1918, **42**, 549—550, 562—564).—In the method of classification proposed, the substances are arranged under chief types depending on the constitution of the

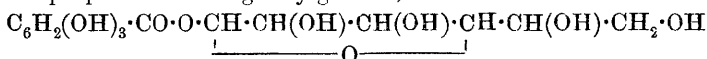
nucleus, these types being subdivided into classes. The types include the quinone type, the diphenylmethane type, the safranine type, the indigo type, etc. Sulphur derivatives and substances of unknown constitution form two separate classes. W. P. S.

Tannin and the Synthesis of Similar Substances. V.

EMIL FISCHER and MAX BERGMANN (*Ber.*, 1918, **51**, 1760—1804. Compare A., 1912, i, 471, 887; 1913, i, 479; 1915, i, 437).—Previous attempts to prepare pentadigalloylglucose did not lead to the desired result, owing to the unfavourable properties of the methylcarbonato-compounds. Recently, however, it has been found possible to prepare the penta-acetyl derivatives of *m*- and *p*-digallic acids and the corresponding chlorides in the crystalline state (A., 1918, i, 172); from these, the penta-(penta-acetyldigalloyl)-glucoses have now been prepared, as well as the corresponding penta-(digalloyl)-glucoses. Penta-(*m*-digalloyl)- β -glucose is shown to be remarkably similar to Chinese tannin, the only point of difference noted being in the specific rotation in aqueous solution. Since, however, the solutions are colloidal in character and their optical activity is greatly influenced by small factors, the authors do not consider the discrepancy is necessarily fundamental.

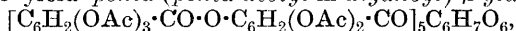
The chemistry of the pentagalloylglucoses has been further studied (compare A., 1915, i, 437), and, through the triacetyl-galloyl derivatives, it has now been found possible to isolate products which consist almost entirely of the pentagalloyl derivatives of α - and β -glucose respectively.

The preparation of 1-galloylglucose,



is also described, this being the first acyl derivative of glucose to which a definite structure can be with certainty assigned. It is in all respects identical with the glucogallin isolated by Gilson from Chinese rhubarb (A., 1903, i, 355).

Penta-acetyl-m-digalloyl [*penta-acetoxy-m-benzoyloxybenzoyl*] chloride, $\text{C}_6\text{H}_2(\text{OAc})_3 \cdot \text{CO} \cdot \text{O} \cdot \text{C}_6\text{H}_2(\text{OAc})_2 \cdot \text{COCl}$, six-sided plates, m. p. 180° (corr.), after slight previous softening, is obtained by the action of phosphorus pentachloride on *m*-digallic acid in the presence of chloroform, and is converted by methyl alcohol in the presence of quinoline into methyl penta-acetyl-*m*-digallate, m. p. 167—168° (corr.) (compare A., 1918, i, 174). It reacts with β -glucose to yield *penta-(penta-acetyl-m-digalloyl)- β -glucose*,



two specimens of which had $[\alpha]_D^{18} + 3.79^\circ$ and $[\alpha]_D^{18} + 2.60^\circ$ in *s*-tetrachloroethane. [*Penta-(penta-acetyl-p-digalloyl)- β -glucose* is obtained in a similar manner; it has $[\alpha]_D^{23} + 1.54^\circ$ (in *s*-tetrachloroethane), and resembles the *m*-derivative so closely that an analytical distinction is almost impossible.] *Penta-(m-digalloyl)- β -glucose* is prepared by deacetylation of the acetyl derivative with cold aqueous sodium hydroxide at 0°, and is purified by means of the *potassium* salt; according to the method of separation, it forms

a pale brown, light, amorphous powder, or a compact, honey-yellow, brittle mass. When hydrolysed by dilute sulphuric acid, it gives approximately the same amount of dextrose and gallic acid as does Chinese tannin. When treated with diazomethane, it yields penta-(pentamethyldigalloyl)-glucose, which, like the earlier preparations, is not perfectly uniform, but which shows a very close analogy with the methyl derivative of the natural Chinese tannin. Reacetylation of penta-(*m*-digalloyl)- β -glucose shows that a certain amount of change (possibly isomerisation of the β -glucose to α -glucose derivative) occurs either during hydrolysis or on treatment with acetic anhydride.

Penta-(penta-acetyl-m-digalloyl)- α -glucose is prepared in the same manner as the β -derivative; individual preparations had $[\alpha]_D + 30.8^\circ$, $+ 27.7^\circ$, and $+ 25.5^\circ$ (in *s*-tetrachloroethane), pointing to admixture with varying amounts of the β -isomeride. [The corresponding *penta-(penta-acetyl-p-digalloyl)- α -glucose* shows the closest analogy with the β -compound] *Penta-(m-digalloyl)- α -glucose* is a pale brown, amorphous powder which can only be distinguished from the β -glucose derivative by its specific rotation; it has $[\alpha]_D^{18} + 43.8^\circ$ (in water), $[\alpha]_D^{18} + 35.8^\circ$ (in alcohol), and $[\alpha]_D^{18} + 40.1^\circ$ (in acetone).

Acetylation of Chinese tannin yields a penta-(penta-acetyldigalloyl)-glucose closely similar to penta-(penta-acetyl-*m*-digalloyl)- β -glucose; the regenerated tannin, however, is found to differ somewhat from the original specimen.

Penta-(triacetyl-galloyl)- α -glucose, $[C_6H_2(OAc)_3 \cdot CO]_5C_6H_7O_6$, is prepared in the usual manner from α -glucose and triacetyl-galloyl-chloride; it forms an amorphous mass, having $[\alpha]_D + 42.7^\circ$ to $+ 46.95^\circ$ in *s*-tetrachloroethane. Deacetylation is accomplished by means of sodium acetate in aqueous acetone solution; the penta-galloyl- α -glucose thus obtained is distinguished from the previous preparation (by hydrolysis of penta-[trimethylcarbonatogalloyl]- α -glucose by alkali) by a considerably higher specific rotation in aqueous and alcoholic solution, but otherwise the resemblance is very close. On treatment with acetic anhydride, the original acetyl derivative is regenerated. Diazomethane converts it into penta-(trimethylgalloyl)- α -glucose, identical with that previously described (*loc. cit.*).

Penta-(triacetyl-galloyl)- β -glucose is a pale yellow, amorphous mass which has $[\alpha]_D^{20} + 5.61^\circ$ or $+ 4.1^\circ$ in *s*-tetrachloroethane; when deacetylated, it yields pentagalloyl- β -glucose, having $[\alpha]_D^{18} + 23.3^\circ$ (in alcohol), $[\alpha]_D^{18} + 13.6^\circ$ and $+ 13.1^\circ$ in 10% and 1% aqueous solution. When treated with diazomethane, it gives a penta-(trimethylgalloyl)- β -glucose which, in its properties and optical activity, closely resembles the preparation previously described (A., 1915, i, 438), but which, unlike the latter, could not be caused to crystallise. Reacetylation yields a product closely resembling the original substance. Hydrolysis of the two penta-(triacetyl-galloyl)-glucoses by alkali at 0° yields α - and β -derivatives respectively, which are quite distinct, although less so than when

sodium acetate is used. (In the case of the corresponding methylcarbonato-compounds, practically identical products were obtained when the hydrolysis was effected by alkali at the ordinary temperature.)

Penta-(p-acetoxybenzoyl)- α -glucose, $[\text{C}_6\text{H}_4(\text{OAc})\cdot\text{CO}]_5\text{C}_6\text{H}_7\text{O}_6$, forms fine needles, m. p. $158\text{--}159^\circ$ (corr.), $[\alpha]_D^{25} + 124.7^\circ$ in *s*-tetrachloroethane; during the preparation, considerable quantities of the β -isomeride are formed, which are removed during purification. The corresponding *penta-(p-hydroxybenzoyl)- α -glucose* could not be caused to crystallise, but the specific rotation of the product ($+163.4^\circ$ in alcohol) was considerably greater than that previously found; on reacetylation, it yielded the crystalline acetyl derivative in excellent yield. The preparation of *penta-(p-acetoxybenzoyl)- β -glucose* and of *penta-(p-hydroxybenzoyl)- β -glucose* is also described, but the substances could not be caused to crystallise, and are probably admixed with the corresponding α -derivatives.

1-Triacetylgalloyl-2:3:5:6-tetra-acetylglucose is prepared from acetobromoglucose and silver triacetyl gallate; it forms microscopic needles or four-sided leaflets, m. p. $125\text{--}126^\circ$ (corr.), after slight softening, $[\alpha]_D^{25} - 24.4^\circ$ in *s*-tetrachloroethane. It may also be obtained from tetra-acetylglucose and triacetylgalloyl chloride. When dissolved in alcohol and treated with ammonia at 20° , it yields *1-monogalloyl- β -glucose*, microscopic, oblique prisms or platelets, m. p. $214\text{--}215^\circ$ (corr.; decomp.), when rapidly heated, $202\text{--}203^\circ$ (corr.; decomp.) when slowly heated; it has $[\alpha]_D^{18} - 25.6^\circ$ in aqueous solution. The product is quite distinct from the glucogallic acid described by Feist (A., 1912, i, 566, 888; 1913, i, 70). When reacetylated, it yields triacetylgalloyltetra-acetylglucose. Its action towards enzymes has been investigated. Its identity with glucogallin is established both by chemical tests and by measurement of the crystals. *1-Galloyl- β -glucosemonoacetate* forms colourless needles, $[\alpha]_D^{18} + 10.5^\circ$ (in alcohol); it has no distinct m. p., but, when rapidly heated, is converted into a viscous, turbid liquid at about 150° after marked softening. *1-Galloyl- β -glucosetetra-acetate* (?) crystallises in needles, m. p. about $136\text{--}137^\circ$, $[\alpha]_D + 38.7^\circ$ (in alcohol), but its isolation in the pure condition is not claimed.

1-Benzoyltetra-acetylglucose is prepared from benzoyl chloride and *2:3:5:6-tetra-acetylglucose*, and agrees in its properties with the product described by Zemplén and László (A., 1915, i, 651) except in specific rotation ($[\alpha]_D^{21} - 26.6^\circ$ in chloroform). *1-o-Acetoxybenzoyl-2:3:5:6-tetra-acetylglucose* crystallises in microscopic, flat prisms. It has m. p. $116\text{--}117^\circ$ (corr.), $[\alpha]_D^{24} - 41.0^\circ$ in *s*-tetrachloroethane. H. W.

Structure of β -Glucosidogallic Acid. EMIL FISCHER and MAX BERGMANN (Ber., 1918, 51, 1804—1808).—The work of Fischer and Strauss (A., 1913, i, 180) has led to the supposition that β -glucosidogallic acid contains the sugar residue attached to the *p*-hydroxyl group of gallic acid; this hypothesis is confirmed by its conversion into glucosyringic acid (Mauthner, A., 1910, i, 667).

Ethyl tetra-acetylglucosidogallate is converted by diazomethane into ethyl tetra-acetylglucosyringate, from which glucosyringic acid is obtained by hydrolysis with barium hydroxide; the free acid has m. p. about 225° (decomp.) when moderately rapidly heated and $[\alpha]_D^{25} - 18.18^{\circ}$ (as sodium salt) in water.

Ethyl triacetylglallate has m. p. $138-139^{\circ}$ (corr.) instead of $132-134^{\circ}$ (A., 1915, i, 683).

Ethyl hexa-acetylglucosidogallate has m. p. $176-177^{\circ}$ (corr.), $[\alpha]_D^{18} - 19.0^{\circ}$ in tetrachloroethane solution. H. W.

Digitalis Substances. XXXVIII. H. KILIANI (*Ber.*, 1918, 51, 1613—1639. Compare A., 1916, i, 493).—The preliminary crystallisation from 85% alcohol is unnecessary in order to separate the digitonin from the gitonin in "crude digitonin amylate" (*Ber.*, 1916, 49, 701). It suffices to dissolve the crude amylate in ten parts of boiling 50% alcohol; on cooling, gitonin material separates first and pure digitonin subsequently.

A sample of "soluble digitonin" supplied by Merck proved to be identical with a new glucoside obtained from the final mother liquor of the crude digitonin (*loc. cit.*).

The sugar syrup previously obtained (*loc. cit.*) could not be made to crystallise, because the sugars in the syrup, which had been produced in an alcoholic medium, are present chiefly in the form of ethyl glucosides. After a second hydrolysis with hydrochloric acid, a partial crystallisation can be effected, and *d*-galactose obtained by inoculation; dextrose, identified as *d*-gluconic acid, is present, and apparently also a third sugar, a ketose, since the syrup is shown to contain oxalic and glycollic acids. (The hydrochloric acid was removed by silver oxide, and it is known that silver oxide acts on hexoses, particularly keto-hexoses, to produce these two acids.)

During the conversion of digitogenin, $C_{31}H_{50}O_6$, into digitogenic acid, $C_{28}H_{44}O_8$, three atoms of carbon are removed. Their fate has not been ascertained; it is shown that they do not appear as acetone, acetaldehyde, malonic, propionic, or carbonic acid.

Digitogenic acid has $[\alpha]_D - 67.1^{\circ}$ in aqueous potassium hydroxide, and forms a *magnesium* salt, $C_{28}H_{42}O_8Mg \cdot 7H_2O$, small, hard nodules of minute needles. β -Digitogenic acid has $[\alpha]_D - 60.2^{\circ}$ in aqueous potassium hydroxide, and forms a *magnesium* salt, microscopic prisms and needles with $7H_2O$. The m. p. of digitogenic acid is altered by crystallisation, and is therefore no safe criterion for identification. The acid is not reduced by hydrogen and colloidal palladium, amalgamated zinc and hydrochloric acid, or zinc dust and acetic acid.

The acid, $C_{16}H_{24}O_7$, obtained by the oxidation of digitogenic acid in about 15% yield (*loc. cit.*), is obtained in about 27% yield by oxidising the amorphous precipitate thrown down by adding water to the mother liquor of the crude digitogenic acid. It is oxidised by potassium permanganate in strongly alkaline solution,

yielding an amorphous *acid*, $C_{15}H_{22}O_7 \cdot H_2O$, decomp. $120-130^\circ$, softening at about 70° , which forms an amorphous *magnesium* salt, $(C_{15}H_{19}O_7)_2Mg_3 \cdot 5H_2O$.

The mother liquor of the crude acid, $C_{16}H_{24}O_7$ (*loc. cit.*), contains, in addition to other substances, at least two very easily soluble acids, one of which has been identified as ethylsuccinic acid.

The oxidation of gitogenic acid by hot chromic, acetic, and sulphuric acids yields an *acid*, $C_{18}H_{28}O_6$, tufts of needles, m. p. 210° , sintering at about 206° (*calcium* salt, $C_{18}H_{26}O_6Ca \cdot 2H_2O$), an *acid*, $C_{19}H_{30}O_6$, m. p. $201-202^\circ$ (*calcium* salt, $C_{19}H_{28}O_6Ca$, amorphous), and ethylsuccinic acid.

Digitoxigenin is not reduced by hydrogen and colloidal palladium, and is oxidised by chromic and acetic acids, yielding a neutral *substance*, $C_{19}H_{26}O_4$, crystals, m. p. 185° .

Digitaligenin forms an *acetyl* derivative, $C_{22}H_{28}O_3Ac_2$, colourless prisms or needles, m. p. $201-202^\circ$ (digitaligenin also has m. p. $201-202^\circ$, not $210-212^\circ$, as stated previously), and is reduced in aqueous methyl-alcoholic solution by hydrogen and colloidal palladium, yielding a *substance*, $C_{19}H_{28} \text{ (or } 30) O_3 \cdot H_2O$, crystals, m. p. $182-184^\circ$, sintering at 175° , which is oxidised by chromic and acetic acids, yielding a neutral *substance*, $C_{19}H_{26} \text{ (or } 28) O_3$, stout crystals, m. p. $190-192^\circ$, and an *acid*, $C_{14}H_{20}O_4$ (by analysis) or $C_{11}H_{16}O_3$ (by titration and by analysis of the *calcium* salt), colourless prisms sintering at $240-245^\circ$ without melting. C. S.

The Isomeric Lactones, Caryophyllin and Urson.

FRANCIS D. DODGE (*J. Amer. Chem. Soc.*, 1918, **40**, 1917-1939).—Comparison of caryophyllin and urson shows a very close similarity of these compounds; in strictly chemical properties no differences have been observed, but the variations in the physical properties appear to warrant the conclusion that they are isomerides of very similar structure. The balance of evidence is in favour of a lactonic constitution, but in certain respects (practically instantaneous neutralisation of alkali in alcoholic solution, opening of lactone ring on acetylation) an unusual behaviour is exhibited.

Caryophyllin is most readily obtained in the pure state through the potassium salt, and crystallises in white needles ($+2H_2O$); the anhydrous substance has m. p. about 310° (corr.), $[\alpha]_D +54.5^\circ$ in alcoholic solution; in a vacuum tube at $280-300^\circ$ it sublimes in characteristic rosettes. The *potassium* salt forms well-defined prisms ($+1.5H_2O$); the anhydrous salt has $[\alpha]_D^{20} +63.4^\circ$ in ethyl alcohol, $[\alpha]_D^{25} +67.7^\circ$ in methyl alcohol. Analyses lead to the formula $C_{30}H_{48}O_4K$ for the salt, and hence to $(C_{10}H_{16}O)_3$ for caryophyllin. The *calcium*, *lead*, *magnesium*, *zinc*, and *silver* salts are described.

Acetylation of caryophyllin under various conditions leads to the formation of *diacetylcaryophyllinic acid* and acetylcaryophyllin; the former substance is somewhat unstable, but can be obtained in the pure state by evaporation of an ethereal solution of the crude acetylation product at the ordinary temperature. It slowly loses acetic acid at the ordinary temperature, and is converted into

acetylcaryophyllin by boiling ethyl alcohol or glacial acetic acid. The *potassium* salt is described. Acetylcaryophyllin forms white, efflorescent needles, m. p. 260—265°, and yields a *potassium* salt which is readily soluble in alcohol. A very sparingly soluble substance, possibly a polymeric acetate, is also obtained during the acetylation of caryophyllin.

Oxidation of caryophyllin with fuming nitric acid yields caryophyllic acid, which is shown to be a somewhat unstable, tribasic acid, $C_{27}H_{45}O_3(CO_2H)_3$, giving a characteristic, sparingly soluble, mono-*potassium* salt. When heated with acetic anhydride it yields a compound, m. p. 210—213° (slight decomp.), which appears to be an acetyl dilactone, $C_{31}H_{46}O_6$, a molecule of carbon dioxide being eliminated during the process.

Urson in its general properties is very similar to caryophyllin. The most striking difference is shown by the potassium salts, that derived from urson being freely soluble in ethyl alcohol, in which the caryophyllin salt is sparingly soluble; a method of separation is based on this dissimilarity. The *lead*, *zinc*, *magnesium*, and *ammonium* (?) salts of urson are described. Urson diacetate (diacetylursonic acid) closely resembles the corresponding derivative of caryophyllin, but is, in general, more soluble and less stable. Decomposition to the mono-acetate occurs so readily that it was found impossible to prepare a pure compound. Acetylurson separates from alcohol in plates or prisms (+ 5H₂O) quite different in appearance from the caryophyllin compound. It was not found possible to purify the product formed by the oxidation of urson with fuming nitric acid. H. W.

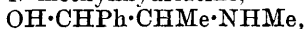
4-Phenylcoumarins. II. ADOLF SONN (*Ber.*, 1918, 51, 1829—1832. Compare A., 1918, i, 401).—Further examples of the formation of 4-phenylcoumarins are given.

Chloroacetylresorcinol dimethyl ether, m. p. 114—115° after softening at 112° [Tambor and du Bois (*A.*, 1918, i, 395) give 119°], is obtained by the action of hydrogen chloride on an ethereal solution of resorcinol dimethyl ether and chloroacetonitrile in the presence of zinc chloride, and is converted by potassium cyanide into *cynoacetylresorcinol dimethyl ether*, prisms or plates, m. p. 152—153°. The latter condenses with phloroglucinol in glacial acetic acid solution under the influence of zinc chloride and hydrogen chloride, yielding 5:7-*dihydroxy-2':4'-dimethoxy-4-phenylcoumarin*, hexagonal prisms, m. p. 232° (decomp.).

Similarly, *cynoacetylcatechol*, m. p. 222° (decomp.), after previous softening, condenses with phloroglucinol to 3':4':5:7-*tetrahydroxy-4-phenylcoumarin*, which, after being purified through the acetyl derivative, forms platelets (+ 2H₂O), m. p. about 270° (decomp.).

H. W.

Improvements in and Relating to Synthetic Drugs [Mydriatic Alkaloids]. NAGAYOSHI NAGAI (*Brit. Pat.* 120936).—Synthetic racemic *N*-methylmydriatine,



or its salts is prepared by the condensation of benzaldehyde with nitroethane by agitation for several hours at the ordinary temperature in the presence of a small quantity of a solution of a weak alkali, such as an alkali carbonate or hydrogen carbonate, or phosphate, or pyridine, etc. The condensation product, phenylnitropropanol, $\text{OH}\cdot\text{CHPh}\cdot\text{CHMe}\cdot\text{NO}_2$, is separated by extraction with ether and freed from benzaldehyde by shaking the ethereal solution with aqueous sodium hydrogen sulphite. The oily residue is dissolved in dilute alcohol, the calculated quantity of formaldehyde is added, and the mixture is reduced at a low temperature by adding dilute acetic acid and zinc dust. The liquid is filtered and the zinc precipitated by hydrogen sulphide; the solution is evaporated in a vacuum and the resinous residue is shaken with dilute hydrochloric acid and ether. The hydrochloride of the base is obtained by evaporating the aqueous layer, and is recrystallised from absolute alcohol. This synthetic ephedrine differs in constitution from Fourneau's ephedrine (A., 1907, i, 762), and is the racemic form of natural ephedrine.

J. F. B.

Alkaloids of the Betel Nut. KARL FREUDENBERG (*Ber.*, 1918, 51, 1668—1682).—Guvacine is 1:2:5:6-tetrahydropyridine-3-carboxylic acid according to the author (A., 1918, i, 403) and 1:2:5:6-tetrahydropyridine-4-carboxylic acid according to Hess and Liebbrandt (A., 1918, i, 401). The author now shows that his view is the correct one by (i) the direct comparison (mixed m. p.'s, etc.) of corresponding derivatives of guvacine and Wohl and Johnson's 1:2:5:6-tetrahydropyridine-3-carboxylic acid, (2) by the identity of *N*-methylguvacine with natural arecaidine, and (3) by a comparison of dihydroguvacine with nipecotinic acid and *isoni*pecotinic acid. Contrary to the statement of Hess and Leibbrandt, dihydroguvacine differs in every way from *isoni*pecotinic acid, and is completely identical with nipecotinic acid (piperidine-3-carboxylic acid). Dihydroguvacine has m. p. 261° (decomp.; corr.), not above 320° , as stated by Hess and Leibbrandt (*loc. cit.*). The nipecotinic acid used by Hess and Leibbrandt was in reality almost pure *isoni*pecotinic acid. Several other errors in their paper are corrected; for example, *N*-methylguvacine (arecaidine, arecaine), when esterified by alcoholic hydrogen chloride, is not demethylated at the nitrogen atom.

C. S.

The Physical Constants of Nicotine. I. Specific Rotatory Power of Nicotine in Aqueous Solution. HARRY JEPHCOTT (T., 1919, 115, 104—108).

Some Derivatives of Pyrrole. IV. G. KARL ALMSTRÖM (*Annalen*, 1918, 416, 279—290. Compare A., 1913, i, 1240; 1915, i, 989; 1916, i, 568).—In some reactions 5-hydroxy-4-acetyl-1:3-diphenylpyrrole (A., 1916, i, 568) behaves as though it were the 5-keto-compound. It is not attacked by boiling alkali hydroxide and benzaldehyde, but by heating with methyl iodide and alcoholic sodium methoxide at 100° yields a mixture of 4-acetyl-1:3-diphenyl-4-

methyl-5-pyrrolone, colourless crystals, m. p. 115—116° (*semicarbazone*, m. p. 217° [decomp.]), and 1:3-diphenyl-4-methyl-5-pyrrolone, colourless needles, m. p. 113—114°. The latter of these is also obtained by heating the former with moderately concentrated sulphuric acid, and is oxidised by chromic and acetic acids to *phenylmethylmaleinphenylimide*, $\begin{matrix} \text{CMe}\cdot\text{CO} \\ | \\ \text{CPh}\cdot\text{CO} \end{matrix} > \text{NPh}$, pale yellow, quadratic plates, m. p. 106—107°, from which aniline and *phenylmethylmaleic anhydride*, m. p. 94—95°, are obtained by boiling with alcoholic sodium ethoxide.

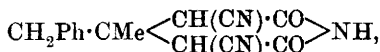
By heating on the water-bath with 2*N*-sodium hydroxide and a large excess of methyl sulphate, 5-hydroxy-4-acetyl-1:3-diphenylpyrrole yields 1:3-diphenyl-4-methyl-5-pyrrolone and 4-acetyl-5-methoxy-1:3-diphenylpyrrole, colourless crystals, m. p. 101°, which forms a *semicarbazone*, pale yellow crystals, m. p. 215° (decomp.), yields 1:3-diphenyl-5-pyrrolone by heating with moderately concentrated sulphuric acid, and is converted into 4-cinnamoyl-5-methoxy-1:3-diphenylpyrrole, yellow crystals, m. p. 111—112°, by heating with aqueous-alcoholic sodium hydroxide and benzaldehyde.

1:3-Diphenyl-4-ethyl-5-pyrrolone, colourless plates, m. p. 118—119°, yields *phenylethylmaleinphenylimide*, yellow, rhombic plates, m. p. 79—80°, by oxidation, from which aniline and *phenylethylmaleic anhydride*, m. p. 46°, are obtained by the action of sodium ethoxide.

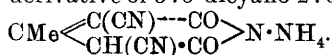
5-Hydroxy-4-acetyl-1:3-diphenylpyrrole does not yield crystalline products by treatment with acetic anhydride, diazomethane, or acetyl chloride, but it reacts with magnesium methyl iodide and then with acetyl chloride to form a substance, $\text{C}_{18}\text{H}_{15}\text{O}_3\text{N}$, colourless needles, m. p. 119—120°. C. S.

General Reaction of Ketones. I. GUARESCHI (*Gazzetta*, 1918, 48, ii, 83—98).—The author has extended his work on the condensation of ketones with ethyl cyanoacetate in presence of ammonia or an amine (A., 1902, i, 819) to benzyl methyl ketone and its homologues in order to ascertain which ketones react incompletely or not at all with the cyanoacetate, and to study the manner in which the new compounds decompose with formation of hydrocarbons.

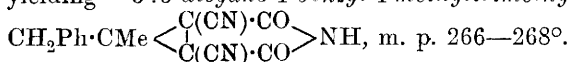
3:5-Dicyano-2:6-diketo-4-benzyl-4-methylpiperidine,



the 1-ammonium derivative of which is formed from benzyl methyl ketone, ethyl cyanoacetate, and ammonia, crystallises in shining needles or prisms, m. p. 255—257°, and has an acid reaction in aqueous solution; its ammonium salt is crystalline, and in aqueous solution decomposes with difficulty into toluene and the ammonium derivative of 3:5-dicyano-2:6-diketo-4-methyl- Δ^3 -tetrahydropyridine,

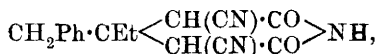


With bromine water 3:5-dicyano-2:6-diketo-4-benzyl-4-methyl-piperidine gives a dibromo-derivative, which, when boiled with alcohol, best with addition of a little formic acid, rapidly loses bromine, yielding 3:5-dicyano-4-benzyl-4-methyltrimethylenedicarbonimide,

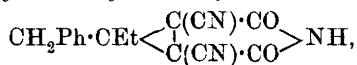


β -Phenylethyl methyl ketone yields 3:5-dicyano-2:6-diketo-4- β -phenylethyl-4-methylpiperidine, which has been already described.

3:5-Dicyano-2:6-diketo-4-benzyl-4-ethylpiperidine,

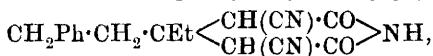


obtained from benzyl ethyl ketone, forms crystals, m. p. 222—226°, which absorb bromine, giving the dibromo-derivative. The latter loses its bromine when boiled with alcohol and formic acid, yielding 3:5-dicyano-4-benzyl-4-methyltrimethylenedicarbonimide,



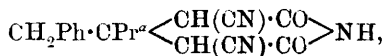
m. p. 226—228°.

3:5-Dicyano-2:6-diketo-4- β -phenylethyl-4-ethylpiperidine,



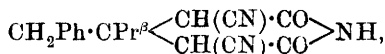
prepared from β -phenylethyl ethyl ketone, forms crystals, m. p. 181—183°.

3:5-Dicyano-2:6-diketo-4-benzyl-4-propylpiperidine,



forms white crystals, m. p. 225°.

3:5-Dicyano-2:6-diketo-4-benzyl-4-isopropylpiperidine,



forms colourless needles, m. p. 248·5—249·5°. When treated with alcohol and formic acid, its dibromo-derivative decomposes, yielding a colourless, crystalline compound, m. p. 255—257°, which is probably 3:5-dicyano-4-benzyl-4-isopropyltrimethylenedicarbonimide.

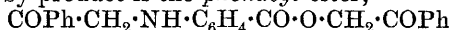
Benzyl isobutyl ketone condenses with ethyl cyanoacetate and ammonia, giving a small quantity of a compound which crystallises in needles, m. p. 223—225°, but was not analysed.

With sodium hydrogen sulphite, benzyl methyl ketone, β -phenylethyl methyl ketone, and benzyl ethyl ketone form crystalline compounds, but this is apparently not the case with β -phenylethyl ethyl ketone or benzyl isobutyl ketone.

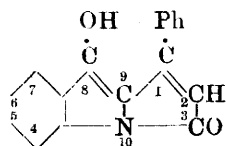
T. H. P.

The Three Phenacylaminobenzoic Acids. M. SCHOLTZ (*Ber.*, 1918, 51, 1645—1653).—The three aminobenzoic acids react with ω -bromoacetophenone in boiling alcohol to form *o*-phenacylaminobenzoic acid, $\text{COPh}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, yellow leaflets, m. p. 190° (*phenylhydrazone*, yellow needles, m. p. 156°), the *m*-isomeride,

colourless crystals, m. p. 202° , and the *p*-isomeride, colourless needles, m. p. 211° respectively. If alkali hydroxide or carbonate also is present in the reaction in the case of the ortho- and para-compounds, a by-product is the *phenacyl* ester,

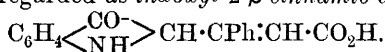


(*o*-ester, hair-like crystals, m. p. 180° ; *p*-ester, colourless needles, m. p. 186°). By treatment with boiling acetic anhydride *m*- and *p*-phenacylaminobenzoic acids are converted into the corresponding *N*-acetyl derivatives, pointed prisms, m. p. 217° , and leaflets, m. p. 176° , respectively, but the ortho-compound is converted into a sub-



stance, $\text{C}_{17}\text{H}_{11}\text{O}_2\text{N}$, colourless needles, m. p. 288° , which is regarded as 8-hydroxy-3-keto-1-phenylpropenylene-2:1-indole (annexed formula). It develops a blood-red coloration with alcoholic ferric chloride, forms a *dibromide*, $\text{C}_{17}\text{H}_{11}\text{O}_2\text{NBr}_2$, pale yellow needles, m. p. 265° , and is converted by hot aqueous

alcoholic potassium hydroxide into the *potassium* salt of an acid, $\text{C}_{17}\text{H}_{13}\text{O}_3\text{N}$, colourless needles, m. p. 300° (decomp.), which does not give a coloration with ferric chloride, forms a *dibromide*, pale yellow needles, and yields a *phenylhydrazone*, yellow needles, m. p. 221° , and is therefore regarded as *indoxyl-2-β-cinnamic acid*,



It is acetylated by warming with acetic anhydride, but the *product*, $\text{C}_{17}\text{H}_{12}\text{O}_3\text{N} \cdot \text{Ac}$, rhombic crystals, m. p. 167° , no longer exhibits the properties of an acid; it regenerates indoxylcinnamic acid after prolonged boiling with aqueous sodium hydroxide.

By boiling with phenylhydrazine in glacial acetic acid all three phenacylaminobenzoic acids yield the *phenylhydrazone* of *s*-phenacylphenylhydrazine, $\text{NHPh} \cdot \text{N} : \text{CPh} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{NHPh}$, yellow needles, m. p. 147° (*acetyl* derivative, $\text{C}_{20}\text{H}_{19}\text{N}_4\text{Ac}$, yellow crystals, m. p. 201°).

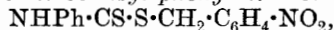
o-Bromoacetophenone and phenylhydrazine react in boiling alcohol to form, not the preceding compound, but a *substance*, $\text{C}_{28}\text{H}_{24}\text{N}_4$, colourless needles, m. p. 174° , which is regarded as *tetra-phenyl-β-tetracarbazone*, $\begin{array}{c} \text{CPh} \cdot \text{CH}_2 \cdot \text{NPh} \cdot \text{N} \\ | \\ \text{N} - \text{NPh} - \text{CH}_2 - \text{CPh} \end{array}$, and is isomeric with the substance, m. p. 137° , obtained by Hess in 1886 from the same two reagents in alcoholic solution at 0° . C. S.

Aldehyde Derivatives of Rhodanines and their Fission Products. I. RUDOLF ANDREASCH (*Monatsh.*, 1918, 39, 419—440).

—A study of the oxidation, reduction, and fission of various condensation products of aldehydes and rhodanines.

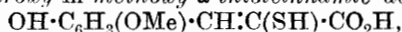
A solution of phenylbenzylidenerhodanine in boiling glacial acetic acid is oxidised by bromine to phenylbenzylidenethiocarbimideglycolide, m. p. 209° (compare A., 1917, i, 663, in which the m. p. is given as 239° in error); similarly, phenyl-*o*-nitrobenzylidenerhodanine yields *phenyl-o-nitrobenzylidenethiocarbimideglycolide*, woolly needles, m. p. 204° .

The following substances have been prepared with a view to the study of their reduction: 5-ethylrhodanine (from ethyl α -bromobutyrate and ammonium dithiocarbamate), yellowish-white, crystalline powder, m. p. 105°; 3-phenyl-5-ethylidenerhodanine, thin, pale yellow plates, m. p. 123°; 3-phenyl-5-ethylrhodanine, pale yellow needles, m. p. 83°; o-nitrobenzyl phenyldithiocarbamate,

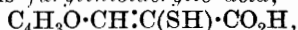


sulphur-yellow needles, m. p. 120—121°. Attempts to reduce ethylidenerhodanine and phenylethylidenerhodanine have not yielded satisfactory results up to the present.

The various aldehyde condensation products of the rhodanines are found to be decomposed with widely differing velocities by alkali; those containing a hydroxy-group in the phenyl residue are particularly resistant, so that, in general, they are only decomposed under conditions which lead to the further degradation of their fission products. The most suitable reagent is a solution of sodium amyl-oxide in amyl alcohol, probably by reason of the higher temperature which can be attained. Under these conditions, phenylpiperonylidenerhodanine yields phenylthiocarbimide and methylenedioxy- α -thiolcinnamic acid, $\text{CH}_2\text{O}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CH} : \text{C}(\text{SH}) \cdot \text{CO}_2\text{H}$, yellow, microscopic needles, which begin to decompose at ca. 170° and are completely molten at 208—210°. The latter acid is transformed by iodine into disulphidobismethylenedioxy-cinnamic acid, m. p. 228°. Similarly, p-hydroxy-m-methoxy- α -thiolcinnamic acid,



pale chrome-yellow, rhombic plates, m. p. 183° after softening at 170°, is obtained from the condensation product of vanillin and phenylrhodanine, whilst the anhydride of o-hydroxy- α -thiolcinnamic acid (m. p. of benzyl derivative, 164—165°) is prepared from phenyl-o-hydroxybenzylidenethiocarbimideglycollide. Phenylfurylidenerhodanine yields furylthiolacrylic acid,



fine needles, m. p. 102—103°, which is transformed by iodine into the corresponding disulphido-acid, lemon-yellow needles or hexagonal plates, m. p. 190—191°. Fission of p-hydroxybenzylidenerhodanine, m. p. 274° after softening at 260°, did not lead to the isolation of p-hydroxy- α -thiolcinnamic acid, but its formation was proved by the separation of its benzyl derivative, colourless, microscopic needles, m. p. 183°. The free acid, chrome-yellow needles, m. p. 186°, was prepared by the action of a solution of sodium amyl oxide in hot amyl alcohol on phenyl-p-hydroxybenzylidenerhodanine, cadmium-yellow needles, m. p. 285°. The corresponding disulphido-acid is a yellow, crystalline powder, m. p. 197°. p-Dimethylamino- α -thiolcinnamic acid has m. p. 160°; the corresponding disulphido-acid is a scarlet powder, m. p. 198°.

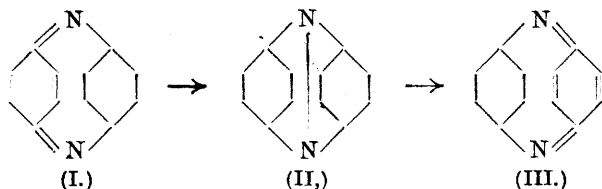
p-Aminobenzylidenerhodanine forms fine, woolly needles resembling chromium trioxide which soften at about 200°, and are not completely melted at 290°; 2:4-diketo-5-p-aminobenzylidenethiazol-

idine, $\begin{array}{c} \text{CO}-\text{S} \\ | \quad | \\ \text{NH}-\text{CO} > \text{C} : \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2 \end{array}$, is a dark reddish-brown powder

which further darkens from about 200° , and has no definite m. p. Attempts to decompose these substances, as also phenyl-*o*-nitrobenzyl-idenerhodanine, by alkali led to negative results. H. W.

Parabanic Acid. ROBERT BEHREND and ADOLF ASCHE (*Annalen*, 1918, **416**, 226—228).—Parabanic acid can be obtained in about 33% yield by rapidly adding 8.4 grams of uric acid to 39 c.c. of nitric acid, D 1.3, heated at 70° , evaporating the solution to dryness, and evaporating the residue two or three times with nitric acid, D 1.4, until the evolution of gas ceases. The product is crystallised from boiling water. C. S.

New Compounds to be employed as Colouring Matters or in the Production of Colouring Matters. ANDREA ANGEL (Eug. Pat., 121347, 1917).—A new type of compounds, for which the name of "parazenes" is suggested, contains two benzene nuclei (or nuclei of benzene derivatives or other cyclic groups) linked together through four para-carbon atoms of the nuclei by two nitrogen atoms. Of the three phases of the formula which may be assigned to parazene, two (I and III) become identical in the absence of unsymmetrical substitution:



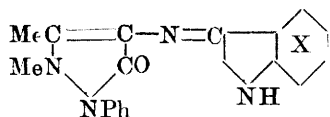
Parazenes are prepared by heating a parahalogen substituted aniline or α -naphthylamine, or derivatives of either containing indifferent groups in the nuclei, with a condensing agent, such as zinc chloride, ferric chloride, aluminium chloride, or phosphoric oxide. The product of the reaction is a hydroxyparazene, which is converted by reduction into parazene. The parazene thus obtained from *p*-chloroaniline is a dark blue powder which, when dissolved in dilute acetic acid, may be used for dyeing wool or silk. Special colouring matters may be produced by introducing auxochromic groups by the ordinary methods. Parazenes will form salts with acids by addition to one or both of the nitrogen atoms. [See, further, *J. Soc. Chem. Ind.*, 1919, February.] C. A. M.

Interaction of Aliphatic Diazo-compounds and Diphenylketen. J. SUREDA Y BLANES (*Anal. Fis. Quim.*, 1918, **16**, 611—624).—With phenyldiazomethane, diphenylketen produces a substance, $C_{21}H_{16}ON_2$, white crystals, m. p. 196° . Diphenyldiazomethane and diphenylketen yield yellow crystals, m. p. 133 — 135° (decomp.). The product from diphenylenediazomethane and diphenylketen is a dark yellow powder, m. p. 157° (decomp.). The constitution of these substances is being further investigated. A. J. W.

Preparation of True Vat Dyes from Di- and Tri-aryl-methane Dyes. HEINRICH WIELAND (D.R.-P. 308298; from *Chem. Zentr.*, 1918, ii, 782—783).—By treatment of the dyes with alkali hyposulphite solution, colourless alkali salts are obtained which are soluble in water, and are reoxidised to the original dyes with extraordinary rapidity by atmospheric oxygen. For example, crystal violet yields sodium hexamethyltriaminotriphenyl-methanesulphonate, $C(C_6H_4 \cdot NMe_2)_3 \cdot SO_3Na$, crystallising in glistening needles.

H. W. B.

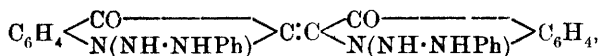
Some Derivatives of Isatin. ANDRÉ MEYER (*Compt. rend.* 1918, 167, 1070—1073).—When the amino-oxindole obtained by the reduction of isatoxime with tin and hydrochloric acid is oxidised by potassium ferricyanide in dilute solution, in addition to isatin, a small amount of a red compound is obtained. If the isatoxime is reduced by zinc and acetic acid, the zinc salt, $C_{16}H_8O_2N_2Zn$, of this red compound is obtained. From its behaviour on reduction with sodium hyposulphite or when dissolved in sulphuric acid, the author considers that the red compound is probably identical with Wahl and Bagard's *isoindigotin*.



Mixed rubazonic acids of the isatin series may be prepared by condensing, in alcoholic solution, amino-antipyrine with isatin, 5-bromoisatin, 5:7-dibromoisatin, and naphthisatin. They have the general constitution (annexed formula), where X represents the substituted benzene or naphthalene nucleus.

W. G.

Derivatives of the Indole and Indigotin Groups Substituted at the Nitrogen Atom. AUGUST ALBERT (*Annalen*, 1918, 416, 240—278. Compare A., 1916, i, 821).—1-Hydroxy-2-thio-3-benzoyloxyoxindole (A., 1915, i, 595) only reacts in the thion form in forming the acetyl derivative. In all other cases, it reacts in the thiol-form, $C_6H_4 \langle \begin{smallmatrix} CH(OBz) \\ NO \end{smallmatrix} \rangle C \cdot SH$. For example, it reacts with phenylhydrazine in cold alcoholic or glacial acetic acid solution to form 2-thiol-3-benzoyloxyoxindolephenylhydrazone hydrate, $NHPh \cdot NH \cdot N(OH) \langle \begin{smallmatrix} C_6H_4 \\ C(SH) \end{smallmatrix} \rangle CH \cdot OBz$, pale yellow plates, m. p. 123—126° (decomp.), which is also formed from the acetyl derivative, acetic acid being eliminated. The phenylhydrazone hydrate is interesting in that the sulphur can be extraordinarily easily eliminated. *N*/2-Sodium hydroxide converts it into 1:1'-bisphenylhydrazinoindigotin,



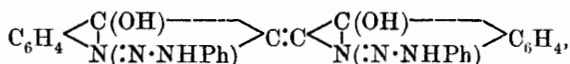
red, rectangular plates, decomp. 237—240°, darkening at 230°, in

which the presence of the two carbonyl groups is shown (1) by heating on the water-bath with aniline or *p*-toluidine and its hydrochloride, whereby the *hydrochloride* of the *anil*,

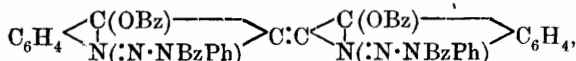
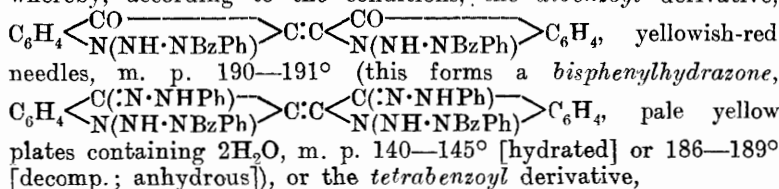


steel-blue needles, decomp. 240° , or of the *p*-tolil, greenish-blue crystals, decomp. $218\text{--}223^\circ$, is obtained, and (2) by heating with phenylhydrazine and its hydrochloride, whereby the *bisphenylhydrazone*, $\text{C}_{40}\text{H}_{34}\text{N}_{10}$, yellow plates, decomp. $200\text{--}206^\circ$, is obtained.

Certain reactions indicate that 1:1'-bisphenylhydrazinoindigotin is able to react in the tautomeric enolic form,



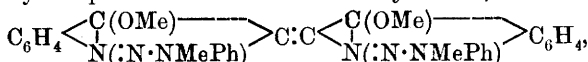
Thus the substance is insoluble in dilute aqueous sodium hydroxide, and is only sparingly soluble in alcohol, but dissolves extremely easily in alcoholic sodium hydroxide, the colour of the solution changing from yellow to blood-red; the yellow colour is regenerated by the addition of water. These colour changes are still more pronounced in the case of the 1:1'-bisphenylmethylhydrazinoindigotin mentioned below; the yellow colour of its alcoholic solution is changed to dark green by alcoholic potassium hydroxide, and is regenerated by the addition of water. The presence of two hydroxyl groups is proved by means of benzoyl chloride. 1:1'-Bisphenylhydrazinoindigotin is boiled with 10*N*-sodium hydroxide until the dark red *sodium* derivative is formed, the mixture is then cooled and treated with benzoyl chloride, whereby, according to the conditions, the *dibenzoyl* derivative,



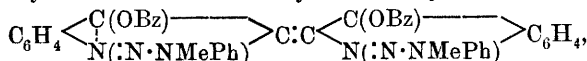
yellow or yellowish-brown, rhombic plates, m. p. $158\text{--}159^\circ$, is obtained. The tetrabenzoyl derivative is converted into the dibenzoyl derivative by careful treatment with sodium ethoxide, and into the bisphenylhydrazone of the latter by warming with phenylhydrazine and its hydrochloride at 50° .

By treatment with *as*-phenylmethylhydrazine, 1-hydroxy-3-benzoyloxy-2-thio-oxindole is converted into a phenylmethylhydrazone, which could not be obtained crystalline, and is readily changed by *N*/2-sodium hydroxide into 1:1'-*bisphenylmethylhydrazinoindigotin*, $\text{C}_{30}\text{H}_{26}\text{O}_2\text{N}_6$, yellow or yellowish-red needles, m. p. 202° (*bisphenylhydrazone*, $\text{C}_{42}\text{H}_{38}\text{N}_{10}$, yellowish-brown plates,

decomp. 165°). This reacts with cold alcoholic potassium ethoxide and methyl sulphate to form the *dimethyl ether*,



dark bluish-red plates, m. p. 105°, and its *sodium* derivative reacts with benzoyl chloride to form only a *dibenzoyl* derivative,



yellow, quadratic plates, m. p. 150—151°. The dibenzoyl derivative is converted into the preceding bisphenylhydrazone, decomp. 165°, by warming with phenylhydrazine, the two benzoyl groups being eliminated.

1:1'-*Bis-p-bromophenylhydrazinoindigotin*, $\text{C}_{28}\text{H}_{20}\text{O}_2\text{N}_6\text{Br}_2$, forms orange-yellow, rectangular plates, m. p. 247° (decomp.), and is converted by warm aniline and aniline hydrochloride into the *hydrochloride* of the *anil*, $\text{C}_{40}\text{H}_{30}\text{N}_8\text{Br}_2 \cdot 2\text{HCl}$, blackish-blue, microscopic plates, m. p. 227—231° (decomp.).

The preceding bisphenylhydrazino- and substituted bisphenylhydrazino-indigotins do not yield vat dyes on reduction, but, undergo profound decomposition, the products depending on the nature of the reducing agent. The course of the reduction in acid media will be described in a later paper. The reduction of 1:1'-bisphenylhydrazinoindigotin suspended in benzene by alcoholic ammonium sulphide yields dihydroindigotin, aniline, and ammonia. Its reduction by *N*-sodium hydroxide and zinc dust in an atmosphere of coal gas for six days yields a pale yellow solution, from which is precipitated by means of atmospheric oxygen a dark blue zinc salt, probably of 1:1'-diaminoindigotin, from which is liberated by dilute hydrochloric acid the *hydrochloride* of *indigotin*-1:1'-

imide, $\text{C}_8\text{H}_4 \cdot \text{N} \cdot \text{NH} \cdot \text{N} \cdot \text{C}_6\text{H}_4$, violet, rectangular plates, decomp.

185°. This base forms an *acetyl* derivative, a very sparingly soluble *sulphate*, $2\text{C}_{16}\text{H}_8\text{O}_2\text{N}_3 \cdot \text{H}_2\text{SO}_4$, needles, and other crystalline salts, and is a true vat dye, yielding with alkaline sodium hyposulphite a yellow vat from which the imide is regenerated by means of oxygen. The preceding zinc salt yields dihydroindigotin by reduction.

C. S.

Compounds Derived from Proteins by Energetic Treatment with Nitric Acid. VII. CARL TH. MÖRNER (*Zeitsch. physiol. Chem.*, 1918, **103**, 80—83. Compare A., 1918, i, 198).—The occurrence of 5-nitroglyoxaline-4-carboxylic and glyoxaline-4-glyoxylic acids, both oxidation products of histidine, among the products of the oxidation of protein, is confirmed (see Knoop, A., 1918, i, 412).

H. W. B.

Hydrolysis of Kafirin. D. BREESE JONES and CARL O. JOHNS (*J. Biol. Chem.*, 1918, **36**, 323—334).—Kafirin, the alcohol-soluble protein of kafir (*Andropogon sorghum*), contains 21.2%

glutamic acid, 15.4% leucine, 8.1% alanine, 7.8% proline, 5.5% tyrosine, 4.3% valine, 3.5% ammonia, 2.3% phenylalanine, 2.3% aspartic acid, 1.6% arginine, 1.1% histidine, 0.95% lysine, and 0.84% cystine. Tryptophan is also present, but glycine is absent. Kafirin therefore closely resembles zein, the alcohol-soluble protein of maize, except in regard to its content of tryptophan.

H. W. B.

Proteins of the Peanut, *Arachis hypogaea*. III. The Hydrolysis of Arachin. CARL O. JOHNS and D. BREESE JONES (*J. Biol. Chem.*, 1918, **36**, 491—500. Compare preceding abstract).—Arachin contains 16.7% glutamic acid, 13.5% arginine, 5.5% tyrosine, 5.3% aspartic acid, 5.0% lysine, 4.1% alanine, 3.9% leucine, 2.6% phenylalanine, 2.0% ammonia, 1.9% histidine, 1.4% proline, 1.1% valine, and 0.9% cystine. Tryptophan is present, glycine absent.

H. W. B.

Chemical Study of Enzyme Action. K. G. FALK (*Science*, 1918, **47**, 423—429; from *Physiol. Abstr.*, 1918, **3**, 407).—The chemical nature of enzymes is discussed in the light of the results of experiments previously published (compare A., 1917, i, 598).

H. W. B.

Studies in Fermentation. III. Pepsin and Peptic Digestion. W. BIEDERMANN (*Fermentforsch.*, 1917, **2**, 1—57; from *Chem. Zentr.*, 1918, ii, 741—742. Compare A., 1917, i, 62).—A suspension of coagulated egg white in water can be employed for detecting a small amount of pepsin. The former is prepared from dried commercial egg albumin by dissolving in water, acidifying with acetic acid, adding sodium chloride, and then heating to the boiling point with continual stirring. The protein separates in very finely divided flocks, which after washing and pressing can be rubbed up with a little glycerol to form a paste, in which form it can be preserved indefinitely. A small fragment about the size of a pea in 10 c.c. of water forms a milky fluid which does not yield a perceptible sediment for several hours. On digestion with a trace of pepsin and hydrochloric acid, the turbidity quickly disappears.

Fibrin is dissolved by dilute hydrochloric acid even in the absence of pepsin. Repeated addition of fibrin results in an increased rate of solution, which appears to indicate that an autolytic or peptic enzyme is closely associated with fibrin or is formed from the fibrin by hydrolysis. If the fibrin is boiled prior to the experiment, it does not dissolve so readily in the dilute acid.

H. W. B.

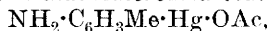
Trypsin, and a New Method of Purifying Enzymes. JOSEPH T. WOOD (*J. Soc. Chem. Ind.*, 1918, **37**, 313—315r).—It has been stated by Holzberg (A., 1913, i, 662) that when a saturated solution of safranin is added to a neutral or very faintly alkaline solution of trypsin, a precipitate is formed which possesses proteolytic properties. This statement is confirmed by the author, and it

is shown that the precipitated material consists of protein matter with the safranine and the enzyme in an adsorbed condition.

Trypsin or other enzyme can be purified by dissolving in a small quantity of water and allowing the solution to soak into filter or blotting paper. After rapid drying at a low temperature, the proteins are retained more tenaciously by the paper than the enzyme, and on placing in water for a few minutes and then filtering, a solution of the enzyme is obtained practically free from protein. Such a protein-free trypsin solution does not give any precipitate with safranine.

H. W. B.

Action of Mercuric Acetate on *p*-Toluidine. I. L. VECCHIOTTI (*Gazzetta*, 1918, **48**, ii, 78—83. Compare A., 1914, i, 1063).—The interaction of mercuric acetate (1 mol.) and *p*-toluidine (1 mol.) yields *p*-toluidinemercuriacetate,



which forms shining, white crystals, m. p. 184° ; the mercuriacetate group probably occupies the ortho-position to the amino-group. The corresponding *hydroxide*, $\text{NH}_2 \cdot \text{C}_6\text{H}_4\text{Me} \cdot \text{Hg} \cdot \text{OH}$, crystallises in pale yellow plates, m. p. 212 — 213° , which begin to turn brown at about 120° ; it renders water strongly alkaline. The *chloride*, $\text{C}_7\text{H}_8\text{NClHg}$, forms prismatic needles, m. p. 170° .

T. H. P.

Physiological Chemistry.

Quantitative Evaporation of Blood Serum. GEORGE H. BURROWS and EDWIN J. COHN (*J. Biol. Chem.*, 1918, **36**, 587—590). —The apparatus consists of an ordinary distilling flask of at least 1 litre capacity supplied with 100 grams of rather large glass pearls. The stopper carries a dropping funnel, the lower end of which extends into the bulb of the flask. The side-tube of the flask is connected with a vertical condenser, which empties into a previously weighed bottle of size suitable for trapping the evaporated and condensed water. Following this in succession is a weighed calcium chloride tower, a manometer, and a vacuum pump. The trap bottle and calcium chloride tower are immersed in ice-cold water, and ice-water should flow through the condenser jacket.

The flask and appendages having been weighed, the apparatus is exhausted to a pressure of 1 cm. of mercury, or less. The flask is immersed in a water-bath at 50°, and the liquid serum is then allowed to enter slowly through the funnel as nearly as possible at the rate at which evaporation proceeds. So treated, the serum foams largely and leaves a friable product which adheres loosely to the walls of the flask. When the desired amount of liquid has been evaporated, the cold water of the condenser jacket is replaced by

warm water and air slowly admitted through the funnel. This is followed by re-exhaustion with slight raising of the temperature of the bath. When the serum is dry, the apparatus is dismantled and the parts weighed. Serum contains about 9% of solids, which, as thus obtained, dissolve readily in water, yielding a slightly turbid solution.

H. W. B.

The Action of Ferric Thiocyanate on Normal Human Serum. ARTHUR VERNES and ROGER DOURIS (*Compt. rend.*, 1918, **167**, 972—974).—The reagent prepared by the action of ammonium thiocyanate or ferric chloride is added to a series of tubes containing 0.4 c.c. of diluted serum, in diminishing dilutions. The first tubes show no precipitation, then follow a series of tubes in which precipitation takes place, and these are followed by another series with no precipitation.

S. B. S.

Mineral Metabolism in Experimental Acidosis. KINGO GOTO (*J. Biol. Chem.*, 1918, **36**, 355—376).—The daily administration of hydrochloric acid to a rabbit during a period of from one to four weeks was accompanied by an increase in the urinary excretion of phosphoric acid. Subsequent investigation showed that the muscles were deficient in phosphorus, sodium, and potassium, and the bones in calcium carbonate. The fat content of the skeleton was also greatly reduced. These results indicate that in acid intoxication after the carbonates in the body fluids have been neutralised, the alkali phosphates of the muscles and the calcium carbonate of the bones are drawn on in the attempt to maintain the hydrogen-ion concentration of the body tissues at the normal level.

H. W. B.

Comparative Metabolism of certain Aromatic Acids.
II. Fate of *p*-Hydroxybenzoic Acid and *p*-Hydroxyphenylacetic Acid in the Organism of the Monkey.

CARL P. SHERWIN (*J. Biol. Chem.*, 1918, **36**, 309—318. Compare A., 1917, i, 603).—Feeding experiments on a monkey (*Macacus rhesus*) indicate that in relation to the process of the metabolism of the aromatic amino-acids, the monkey stands in the same position as other lower animals and thus differs from man. The monkey excretes the *p*-hydroxybenzoic acid in the urine in an uncombined state, whilst a partial combination with glycine takes place in the human organism. On the other hand, *p*-hydroxyphenylacetic acid is partly excreted as *p*-hydroxyphenylaceturic acid in the case of the monkey and lower animals, but is excreted in an uncombined form in man.

H. W. B.

Metabolic Changes induced by the Administration of Guanidine Bases. V. **Change of Phosphate and Calcium Content in Serum in Guanidine Tetany and the Relation between the Calcium Content and Dextrose in the Blood.** C. K. WATANABE (*J. Biol. Chem.*, 1918, **36**, 531—546. Compare A., 1918, i, 327).—The administration of guanidine to rabbits produces a condition of severe acidosis with the retention of phosphates, a

decrease of calcium in the blood, and a hypoglycæmia. After the extirpation of the parathyroids in the rabbit, phenomena and symptoms are observed which are similar to those occurring after the administration of guanidine. Since there is a large increase in the guanidine bases in the blood in parathyroid and in idiopathic tetany, it is possible that the fundamental cause of tetany is the increased formation of guanidine brought about by the disturbance of the function of the parathyroids.

H. W. B.

Influence of Protein Feeding on the Concentration of Amino-acids and their Nitrogenous Metabolites in the Tissues. H. H. MITCHELL (*J. Biol. Chem.*, 1918, **36**, 501—520).—

The concentration of amino-acids, ammonia, and urea in the tissues of rats is comparable to that in the tissues of other mammals. In the young, growing animal the concentration of the amino-acids in the tissues is considerably higher than in the adult animal, due possibly to the greater metabolic activity of the young as compared to the adult tissues. The effect of feeding with protein depends also on the age of the animal; in young rats the concentration of the amino-acids and urea in the tissues is increased, whilst in the adult animal no or only a slight increase can be detected.

H. W. B.

Animal Calorimetry. XV. Further Experiments Relative to the Cause of the Specific Dynamic Action of Protein.

H. V. ATKINSON and GRAHAM LUSK [with G. F. SODERSTROM] (*J. Biol. Chem.*, 1918, **36**, 415—427. Compare Lusk, A., 1915, i, 614).—The administration of hydrochloric acid to a dog causes a slight increase in the basal metabolism, but a further increase is not observed when aspartic acid is simultaneously given. Aspartic acid, like glutamic acid, does not therefore exert any specific dynamic action. Asparagine and glycine behave very differently in metabolism, the former being without specific dynamic action, whilst the latter exerts the most powerful specific dynamic action of any of the amino-acids in protein which have been thus far tested. Therefore, the hypothesis of Grafe (*Deutsch. Arch. Klin. Med.*, 1915, **118**, 1) that the specific dynamic action of protein is due to the amino-radicles of the amino-acids is shown to be incorrect. Neither succinic acid nor acetamide is found to increase the heat production of the animal. The authors draw the conclusion that the processes of deamination and urea formation have nothing to do with the specific dynamic action of protein.

H. W. B.

Penetration of Neutral Salts into [Animal] Cells. WILHELM VON MOELLENDORFF (*Kolloid Zeitsch.*, 1918, **23**, 158—163).—A number of experiments on the penetration of solutions of sodium chloride, manganese sulphate, uranium nitrate, and potassium sulphate into liver and kidney cells of animals are described. The experiments show that sufficient of the salts penetrate to produce an intracellular precipitation of the acid colour substances contained in the cells. This precipitation is identical with the action of neutral

salts on semi-colloids and is characterised as a diminution of the dispersion. The process indicates that the cell walls are permeable to neutral salts. The process is in keeping with the theory of a sponge-like structure for protoplasm. J. F. S.

Synthetic Capacity of the Mammary Gland. I. Can this Gland Synthesise Lysine? E. B. HART, V. E. NELSON, and W. FITZ (*J. Biol. Chem.*, 1918, **36**, 291—307).—Rats fed on a lysine-free diet of zein and tryptophan with non-nitrogenous substances are able to give birth to their young, but appear to be unable to rear them. It is considered that these results are due to the failure of the mammary glands of the rats to produce sufficient milk, owing to the absence of the lysine necessary for the formation of the protein normally present in rat's milk. H. W. B.

Vitamine Studies. II. Does Water-soluble Vitamine Function as a Catalase Activator? R. ADAMS DUTCHER and FERDINAND A. COLLATZ (*J. Biol. Chem.*, 1918, **36**, 547—550. Compare A., 1918, i, 561).—Vitamine extracts do not increase the catalytic activity of extracts of liver. The vitamine in the body does not act as a direct activator of catalase, but seems to stimulate the organism to greater production of the enzyme. H. W. B.

Vitamine Studies. III. Curative Properties of Honey, Nectar, and Maize-pollen in Avian Polyneuritis. R. ADAMS DUTCHER [with L. V. FRANCE] (*J. Biol. Chem.*, 1918, **36**, 551—555. Compare preceding abstract).—Honey contains a small amount of the water-soluble vitamine, but the amount is so small that its curative effect can only be observed after concentration of the vitamine by adsorption with siliceous earth. Nectar appears to be almost free from vitamines, but maize-pollen is relatively rich in this respect, small amounts of pollen extract being sufficient to cause the recovery of pigeons in the last stages of polyneuritis. It is possible that it is the presence of pollen grains in ordinary honey which confers on it its small curative power over polyneuritis. H. W. B.

Quinine in Animal Tissues and Liquids, with Methods for its Estimation. W. RAMSDEN, I. J. LIPKIN, and E. WHITLEY (*Ann. Trop. Med. Parasitol.*, 1918, **12**, 223—258. Compare Ramsden and Lipkin, A., 1918, ii, 251; Hartmann and Zila, A., 1918, i, 328).—The method previously described by Ramsden and Lipkin is applicable to the estimation of quinine in most tissues, but not in liver and brain. Given in large doses, the alkaloid accumulates in most tissues (particularly the suprarenals and kidneys) much more than in the blood, where three-fourths is in the serum but scarcely any in the red corpuscles; 90% of an intravenous dose leaves the blood in the first minute after injection. Quinine resists putrefaction in urine and fæces, but is rapidly attacked post mortem by the liver, presumably in a manner identical with the normal fermentative process of quinine metabolism during life. In a succession of large doses by the mouth more than 90% may be so metabolised. In

man there is considerable idiosyncrasy, both as regards the rate of excretion and the concentration in the blood; high concentration in the blood is associated with the symptoms of quinine intoxication. Quinotoxine is attacked by the liver like quinine, but some at least is excreted unchanged by the urine. G. B.

Creatinuria. I. Exogenous Origin of Urinary Creatine.

H. STEENBOCK and E. G. GROSS (*J. Biol. Chem.*, 1918, **36**, 265—289).—Experiments on pigs are described, the results of which indicate that creatine is formed from a precursor or precursors in the protein molecule. Urinary creatine has an exogenous origin only when the protein in the food happens to contain a large proportion of the creatine precursor. Feeding with excess of a protein containing a relatively small proportion of the creatine precursor may result in an inhibition of the production of creatine, on account of the accompanying diminution in protein katabolism effected by the agency of the non-nitrogenous portion of the protein of the food. In the discussion of the results attempts are made to reconcile the numerous apparently contradictory conclusions arrived at by other workers on this subject. H. W. B.

Method for the Identification of certain Carbamido-acids in the Presence of Amino-acids and of Urea. ALICE RÖHDE (*J. Biol. Chem.*, 1918, **36**, 467—474).—The method consists in decomposing the urea by urease, and then extracting the carbamido-acids, after acidifying with phosphoric acid, by means of ethyl acetate. The extract is then distilled with steam and the aqueous residue clarified with charcoal and then concentrated to small bulk. The crystals of carbamido-acid which separate are identified by the melting point, etc.

A method for the quantitative estimation of these acids by the Van Slyke process is based on the fact that the anhydrides formed from them are not decomposed by nitrous acid. The difference in the volumes of gas evolved before and after boiling the carbamido-acid solution with hydrochloric acid is a measure, therefore, of the amount of carbamido-acid present.

Applying these methods, it is found that after the injection of amino-acids into cats, carbamido-acids cannot be detected in the urine, whilst injected carbamido-acids are excreted in an unaltered form. Conjugation of amino-acids with urea preparatory to excretion does not seem, therefore, to occur in the animal organism.

H. W. B.

Chemistry of Vegetable Physiology and Agriculture. •

Autolysis of Starch. W. BIEDERMANN (*Fermentforsch.*, 1918, 2, 200; from *Chem. Zentr.*, 1918, ii, 738. Compare A., 1917, i, 62).
 —Boiled starch solutions after some weeks become infected with a bacterium which forms a sulphur-yellow pigment and hydrolyses

the starch to dextrose. The bacterium is possibly identical with, or at least closely related to, Schardinger's *Bacillus macerans*. The previously recorded autolysis of starch was probably due to infection with this micro-organism. H. W. B.

Azofication. J. E. GREAVES (*Soil Sci.*, 1918, **6**, 163—217).—A résumé of the literature on the subject of nitrogen fixation by *Azotobacter* and *Clostridium pasteurianum*. A full bibliography is appended. W. G.

Influence of certain Conditions on the Comparative Consumption of Dextrose and Lævulose by Sterigmatocystis nigra, starting from Sucrose. MARIN MOLLIARD (*Compt. rend.*, 1918, **167**, 1043—1046).—Using a culture liquid in which the nitrogen is entirely supplied by one ammonium salt and the ratio nitrogen:carbon is 1:16, it is found that the ratio of dextrose to lævulose consumed is considerably increased by the presence of acid. Similarly, the ratio dextrose to lævulose consumed is increased if the ratio nitrogen:carbon is diminished to 1:160. In each of these cases, the weight of mycelium obtained in a given time is also diminished. It is considered that lævulose plays the principal part in the building up of the tissues. W. G.

Capacity of Alcohols and Acids to Sustain the Growth of Yeasts and other Common Fungi. TH. BOKORNY (*Allg. Brau Hopf. Zeit.*, 1917, 747; from *Bied. Zentr.*, 1918, **47**, 191).—The author has collected information regarding the behaviour of fungi, yeasts, and bacteria when cultivated in media containing various alcohols and acids. All acids exert an inhibiting action on fermentation when the concentration is increased to a certain limit, which differs for each substance. Formic and oxalic acids are specially toxic. Bases are more poisonous than acids towards yeast. H. W. B.

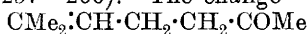
Quantitative Estimations of the Enzymic Activity of Living Cells. I. H. EULER, O. SVANBERG, and S. HEINTZE (*Fermentforsch.*, 1918, **2**, 194—199; from *Chem. Zentr.*, 1918, ii, 746).—At 16°, an increase in p_H from the optimum for yeast invertase (5.07 to 4.67) to 7.7 reduces the activity of the invertase from 0.067 to 0.007. H. W. B.

Influence of certain Substances Extracted from Yeast by Alcohol on the Activity of the Yeast Enzymes. EMIL ABDERHALDEN and H. SCHAUMANN (*Fermentforsch.*, 1918, **2**, 120—151; from *Chem. Zentr.*, 1918, ii, 737—738).—An extract of yeast, prepared by boiling with 10% sulphuric acid and subsequently treating with alcohol, exerts an accelerating action on the enzymic cleavage of sucrose and maltose and on the fermentation of dextrose, lævulose, and particularly galactose by yeast. The fermentation of lactose is not affected. The activity of carbonylase is increased. The accelerative action of the extract is observed, not only with living yeast, but in the cases of dried yeast and pressed yeast juice. Various fractions can be prepared from

the extract possessing diverse degrees of activating power, one of the more powerful being termed "eutonin." This latter substance is prepared by precipitation of the alcoholic extract with acetone, and is completely free from phosphorus. The author suggests that vitamins may resemble these extracted substances in exerting an activating influence on certain enzymic processes in the body.
H. W. B.

Behaviour of Yeast towards various Carbohydrates in various Concentrations, and the Effect of the Addition of Amino-acids on the Fermentation. EMIL ABDERHALDEN (*Fermentforsch.*, 1916, 229; from *Bied. Zentr.*, 1918, 47, 190).—The extent of alcoholic fermentation is not affected when the concentration of the sucrose in the solution is increased from 10 grams to 30 grams per 250 c.c. The loss in weight is greater when alanine is added to the sucrose solution. When dextrose is substituted for sucrose, the extent of fermentation is found to vary with the concentration of the carbohydrate. When dried yeast is employed, a distinct latent period precedes the onset of fermentation.
H. W. B.

Phytochemical Reductions. XIV. Hydrogenation of a Ketone by Yeast. Change of Methylheptenone into the Corresponding Heptenol. C. NEUBERG and A. LEWITE (*Biochem. Zeitsch.*, 1918, 91, 257—266).—The change



into $\text{CMe}_3\text{:CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OH}$ takes place to the extent of about 10%. The product is sometimes levorotatory and at other times dextrorotatory. There is produced at the same time an equimolecular proportion of acetaldehyde. The ketone appears to compete with this product, formed as an ordinary intermediary product of alcoholic fermentation, for the available hydrogen.

S. B. S.

Excitation of Ferment Action. WOLFGANG WEICHARDT and HERMANN APITZSCH (*Biochem. Zeitsch.*, 1918, 90, 337—347).—A criticism of certain statements in literature with regard to excitation of ferment action, with some demonstrations of sources of error in methods of manipulation in experiments on which certain statements are founded. These refer more especially to the measurement of catalase action volumetrically, to the difficulties of measuring the same amounts of catalase (or blood), and to the errors in the estimation of the action of urease due to the neglect of hydrolysis of carbamide while distilling off the ammonia.
S. B. S.

The Influence of Aluminium on the Germination of Seeds and the Development of Plants. JULIUS STOKLASA with J. ŠEBOR, W. ZDOBNICKY, F. TÝMICH, O. HORÁK, A. NĚMEC, and J. CWACH (*Biochem. Zeitsch.*, 1918, 91, 137—223).—This communication contains a very detailed account of the action of aluminium, manganese, and iron on the germination of seeds and the development of the plants. It indicates, generally, that very

small amounts of aluminium salts exert a favourable influence on the germination of seeds, whereas larger amounts exert a toxic action. Similar remarks apply to salts of manganese. When large amounts of manganese salts exert a toxic action, an antagonistic effect can be produced by aluminium salts when the concentration of the latter is not too high, and the toxic effect of both ions comes into play. A study of the action of these various salts when used in the nutrient solutions for growing plants indicated that aluminium is very toxic to xerophytes, whereas the hydrolytes and hygrophils show a considerable resistance. As regards the mesophytes, a toxic action could be determined in the case of iron ions which could be antagonised by aluminium. Aluminium and manganese ions in sufficiently low concentrations, both together or alone, produce a favourable effect on growth; higher concentrations act toxically. There is no antagonistic action as regards toxicity of iron and manganese. The authors deduce from their results a mathematical expression for the growth curves, and develop a general theory of the action of chemical reagents on growth. Measurements were made of the electrical conductivities of the salts employed, and comparisons instituted between the intensity of action of the various ions and the dissociation grade of the salts; a considerable parallelism was found to exist between this physiological intensity of action and the conductivities of the salt solutions.

S. B. S.

Catalase and Oxydase Content of Seeds in Relation to their Dormancy, Age, Vitality, and Respiration. WILLIAM CROCKER and GEORGE T. HARRINGTON (*J. Agric. Res.*, 1918, 15, 137—174).—The concentration of solutions of hydrogen peroxide may readily be measured by determining the volume of oxygen liberated on the addition of an excess of powdered seeds containing plant catalase. Similarly, the catalase activity of seeds may be measured by using an excess of hydrogen peroxide, but in this case the latter solution must first be made neutral to phenolphthalein by the addition of *N*/10-sodium hydroxide. The authors have carried out a general investigation as to the conditions affecting catalase and oxydase activity of seeds, and find that in certain seeds there is a close correlation between catalase activity and respiratory intensity, but no correlation between these two factors and the vitality of the seeds or the vigour of the resulting seedlings. They find that general conclusions cannot be drawn as to the catalase behaviour in all seeds, but it seems probable that seeds can be separated into several physiological types, for each of which more or less general conclusions can be drawn. Catalase activity of seeds seems to agree more closely and generally with physiological behaviour than does oxydase activity. [See, further, *J. Soc. Chem. Ind.*, 1919, February.]

W. G.

Distribution of the Mineral Elements and Nitrogen in the Etiolated Plant. G. ANDRÉ (*Compt. rend.*, 1918, 167, 1004—1006).—The author has investigated the proportions of

mineral matter and nitrogen which pass, during etiolation, from the cotyledons into the plantule in seeds germinated in the dark in an inert medium. The seeds used were white haricot, germinated in sand previously extracted with acid and calcined. After twenty-five days, the stems being 30—35 cm. in length, the plants were removed and their roots washed. Their cotyledons were separated from the stem and roots and weighed separately, and then analysed. The major portion of the calcium remained in the cotyledons, whilst the magnesium, and to a still greater extent the potassium, had migrated to the roots and stem. Nearly 75% of the phosphoric acid and nitrogen were transported from the cotyledons to the plantule, and the migration of the sulphur was very similar.

W. G.

Mechanism of Assimilation Processes. K. SCHAUM (*Ber.*, 1918, **51**, 1372—1375).—The conclusions recorded by Willstätter and Stoll (*A.*, 1918, i, 207) had been drawn previously by the author (*Sitzungsber. Ges. Beförd. gesamt. Naturwiss. Marburg*, 1907, 158).

C. S.

Colloidal Properties of Protoplasm. Imbibition in Relation to Growth. FRANCIS E. LLOYD (*Trans. Roy. Soc. Canada*, 1917—18, [iii], **11**, 133—139).—Living protoplasm, as such, behaves towards acids and alkalis in a manner sufficiently like that of gelatin to warrant the view that imbibition is a factor in growth. The results in growth are called forth by much lower concentrations of the reagents; this is probably due to the different nature of the emulsoids involved.

J. F. S.

Conductivity as a Measure of Permeability. W. J. V. OSTERHOUT (*J. Biol. Chem.*, 1918, **36**, 485—487).—Experiments are described which are designed to elucidate whether when an electric current passes through a tissue, any of the current passes through the protoplasm or all through the intercellular substance. Employing a green marine alga (*Ulva*) and a marine flowering plant (*Zostera*), both with cellulose walls, it is found that after killing by methods which do not produce irreversible changes in the properties of cellulose, the conductivity rises to a constant value and is not thereafter affected by exposure to reagents which produce great alterations in the conductivity of living tissues. Moreover, the temperature-coefficient of the electrical conductivity of living tissue differs from that of dead tissue, and the effect of placing a tissue in contact with a strong calcium chloride solution is not an increase in the conductivity, but a decrease on account of the diminished conductivity of the protoplasm killed by the salt more than counterbalancing the increased conductivity of the intercellular tissues. The alterations of conductivity observed in living tissue are due, therefore, to changes in the protoplasm, and not to changes in the non-living intercellular substance, and as the results obtained by the electrical method are in complete agreement with those obtained by other methods for measuring permeability, such as exosmosis.

diffusion through membranes of living tissue, etc., the author draws the conclusion that the electrical conductivity is a measure of the permeability of the protoplasm of the cell. H. W. B.

Effect of Diffusion on the Conductivity of Living Tissue. W. J. V. OSTERHOUT (*J. Biol. Chem.*, 1918, **36**, 489—490).—Electrolytes with univalent cations usually produce an increase in the electrical conductivity of living tissues, whilst those with bi- or ter-valent cations first diminish and then increase the conductivity. Certain apparent exceptions to this rule have been noted, and these are now shown to be due to the effect of diffusion. Thus, on transferring tissue of *Laminaria* from sodium chloride to rubidium chloride solution of the same conductivity, the molecules of sodium chloride diffuse out of the tissue more rapidly than the larger molecules of rubidium chloride can diffuse inward. Hence there is a temporary deficiency of salt in the tissue, and the conductivity accordingly falls. Reverse effects are produced on transference into lithium chloride solutions. H. W. B.

Method of Measuring the Electrical Conductivity of Living Tissues. W. J. V. OSTERHOUT (*J. Biol. Chem.*, 1918, **36**, 557—568).—Various types of apparatus are figured and described which permit of the measurement of the electrical conductivity of pieces of living tissue or of intact organisms. Successive measurements do not vary more than 1% from the mean value. H. W. B.

The Absorption Curve of the Green Colouring Matter in Living Leaves. A. URSPRUNG (*Ber. Deut. bot. Ges.*, 1918, **36**, 73—85).—The absorption curve has been determined by the thermoelectric method for the green pigments in a living leaf of *Tradescantia*. A very slight absorption occurs in the green part of the spectrum, which increases towards the red and the violet ends, reaching a maximum in the violet, which is greater than that occurring in the red. Towards the red end of the spectrum the absorption curve reaches a maximum point between *B* and *C*, and then falls rapidly towards the ultra-red. H. W. B.

Significance of the Wave-length for Starch-formation [in the Green Leaf]. A. URSPRUNG (*Ber. Deut. bot. Ges.*, 1918, **36**, 86—100. Compare preceding abstract).—A comparison of the absorption curve with one indicating the extent of formation of starch in the green leaf reveals a close parallelism extending from the ultra-red to the green part of the spectrum. From this point towards the violet, marked divergence is observed; the absorption increases to a maximum, whilst the starch-formation greatly diminishes. It is probable that the latter phenomenon is occasioned by the action of the ultra-violet light on the stomata, which results in the reduction of the supply of carbon dioxide for photo-synthetic purposes. In a few experiments with leaves containing no stomata,

the parallelism between absorption and starch-formation could be established as far as the bluish-violet part of the spectrum.

H. W. B.

Microchemistry of Plants. X. Siliceous Bodies in the Epidermis of *Campelia Zanonia*, Rich. XI. Crystalline Carotin in the Cup of *Narcissus poëticus*. HANS MOLISCH (*Ber. deut. bot. Ges.*, 1918, **36**, 277—281, 281—282).—Siliceous bodies, similar to those discovered by Möbius (*Wiesner-Festschrift*, Vienna, 1908, p. 81) in the leaves of *Callisia repens*, are present in the epidermis of *Campelia Zanonia*. They occur in small cells in the leaves and stalks, and are insoluble in acids, except hydrofluoric acid. When the leaf is immersed in phenol solution or in Millon's reagent, the bodies assume a peculiar red hue, which renders them very apparent. These two *Commelineæ*, therefore, are related, not only botanically, but also in a pronounced chemical manner.

The red colour in the rim of the cup of *Narcissus poëticus* is found to be due to the presence of accumulations of carotin crystals in the cells.

H. W. B.

The Phenol of the Leaves of *Coleus amboinicus*, Lour (*C. Carnosus*, Hassk.). F. WEEHUIZEN (*Rec. trav. chim.*, 1918, **37**, 355—356; *Pharm. Weekblad*, 1918, **55**, 1470—1472).—The essential oil of *Coleus amboinicus* contains a phenol which the author has identified as carvacrol.

W. G.

Presence of Hydrogen Cyanide in a Fern, *Cystopteris alpina*. MARCEL MIRANDE (*Compt. rend.*, 1918, **167**, 695—696).—The fern, *Cystopteris alpina*, Desv., contains in its leaves a cyanogenetic glucoside which under the influence of an enzyme, also contained in the plant, is hydrolysed, and yields hydrogen cyanide and benzaldehyde. The proportion of hydrogen cyanide given by the leaves is lowest in the early part of September (for example, 0·011%).

C. A. M.

Production of Glycine by *Isaria densa*. MARIN MOLLIARD (*Compt. rend.*, 1918, **167**, 786—788).—The fungus *Isaria densa*, when cultivated on gelatin decomposes it, giving glycine, the yield of this amino-acid being equivalent to 33% of the gelatin decomposed, whereas by acid hydrolysis gelatin only yields 16·5% of glycine. Similarly, this fungus decomposes fibrin, giving 38% of glycine, and also ovalbumin, serum-albumin, and casein, giving on an average 33·6% of glycine.

W. G.

Sterilised Poppy Juice. L. REUTTER DE ROSEMONT (*Schweiz. Apoth. Zeit.*, 1918, **56**, 55—56; from *Chem. Zentr.*, 1918, ii, **89**, 736—737).—The results indicate that certain alkaloids exist preformed in poppy juice and are not the products of subsequent fermentation processes. On distillation in a vacuum, poppy juice

gives off formic and acetic acids, and, after subsequent treatment with sodium hydroxide, ammonia, pyrrolidine, and methylpyrrolidine. By extraction of the tarry residue, several basic substances, including codeine but not morphine, are obtained. Light petroleum extracts pyrrolidine, benzene, a yellow *liquid*, $(C_8H_3O_4N)_x$, *aureichloride*, m. p. 231° , chloroform, a yellowish-brown *powder*, $(C_3H_7O_5N)_x$, and amyl alcohol, a solid *alkaloid* $(C_2H_3O_5N)_x$. The residue is soluble in dilute hydrochloric acid, and from the solution sodium hydroxide precipitates a colourless *substance*, $(CHO_3N)_x$. Lactic, meconic, and oxalic acids, together with dextrose, were also detected in the original juice. H. W. B.

Vegetable and Animal Fats and Waxes. II. ALBERT B. WEINHAGEN (*Zeitsch. physiol. Chem.*, 1918, **103**, 84—86. Compare A., 1918, i, 56).—The solid fat isolated from rice bran does not contain any glycerol, whilst the liquid oil contains only about 1.7%. H. W. B.

Oxydases: with Special Reference to their Presence and Function in the Sugar-cane. RAMJI NARAIN (*Agric. J. India*, 1918, 47—64).—Laccases and aldehydase are found to be present in the cane, but tyrosinase is absent. The author finds that the direct guaiacum reaction depends more on the presence of a peroxide than on that of catechol. As a preservative for oxydases, chloroform is far more satisfactory than either ether or toluene. In the cane the lower portions show a greater oxydase activity than the upper portions, and thus the oxydases are stronger in that part of the plant where the sugar is stored. Similarly, the leaf and the adjoining green portion of the cane are richer in oxydase than the stem. The oxydases are not destroyed by boiling the extract containing them for fifteen minutes, although they take some time to recover their activity after cooling. Similarly, a reducing agent such as hydrogen sulphide only temporarily inhibits their activity but does not destroy it permanently. The author considers that oxydases are not enzymes in the true sense of the word. W. G.

Gaseous Products of the Putrid Fermentation and the Odour of Truffles. I. GUARESCHI (*Gazzetta*, 1918, **48**, ii, 98—106).—The gaseous or highly volatile products emitted during the putrefaction of truffles are mostly absorbable by soda lime (compare A., 1916, ii, 324, 562). Those not so absorbed have the odour of the fresh truffle, such odour being due to one or more gases or volatile compounds, which are formed by the putrefactive alteration of the proteins, but are not yet identified. T. H. P.

Action of Coal Gas on Plants. IV. Action of Coal Gas on the Root Systems of Trees. Cause of the Action of the Gas. C. WEHMER (*Ber. Deut. bot. Ges.*, 1918, **36**, 140—150. Compare A., 1917, i, 618).—The experiments on the effects produced by passing gas through soil containing the roots of plants have been

extended to small trees in pots. It is found that the effect produced is dependent on the season of the year in which the experiment is performed; it completely kills the tree in the spring; in autumn the leaves fall off, but the tree remains alive, whilst in winter no pernicious effect is observable. When the soil is replaced by a solution of salts, similar toxic effects are observed. The toxicity appears to be due to one or more constituents of the gas, and not to mere absence of oxygen. Any treatment of the gas which removes its peculiar odour also abolishes its toxicity, a result which seems to show that the toxic agent is that constituent of the gas which confers on it its characteristic odour.

H. W. B.

Soil Acidity as Affected by Moisture Conditions of the Soil. S. D. CONNER (*J. Agric. Res.*, 1918, **15**, 321—329).—The acidity of acid soils, kept under different conditions of moisture in pots for a year, varied with the different conditions of moisture for a given soil. Soils rich in organic matter showed the greatest acidity after being kept fully saturated, whilst soils poor in organic matter showed the greatest acidity after being kept half-saturated. The potassium nitrate extract from the fully saturated soils contained more soluble ferrous iron and manganese, but less aluminium, than the other soils. Thus the measurable acidity of acid soils varies to a large degree under different conditions of moisture and aeration, but this variation is due to chemical rather than to physical changes in the soil.

W. G.

Determining the Absolute Salt Content of Soils by Means of the Freezing-point Method. GEORGE J. BOUYOUKOS and M. M. MCCOOL (*J. Agric. Res.*, 1918, **15**, 331—336).—The authors find that at a comparatively high content of moisture, the influence of the unfree water on the concentration of the soil solution is practically negligible. The freezing-point method can therefore be used to determine the absolute salt content of soils by bringing them to a suitable content of moisture before determining the depression of the freezing point. [For details, see *J. Soc. Chem. Ind.*, 1919, February.]

W. G.

Hydrogen-ion Concentration—Soil Type—Common Potato Scab. LOUIS J. GILLESPIE and LEWIS A. HURST (*Soil. Sci.*, 1918, **6**, 219—235).—The authors find that the electrometric method (compare Gillespie, A., 1916, i, 303) and the colorimetric method of Clark and Lubs (compare *J. Bact.*, 1917, **2**, 1, 109, 191) for determining hydrogen-ion concentration of soils give results which are in agreement within the limits of experimental error. It is necessary to add 1 or 2 c.c. of water to each gram of air-dry soil, but this addition of water does not seem to be a serious limitation. From an examination of a large number of soils the authors find a close correlation between the hydrogen-ion exponent and the occurrence of common potato scab. With an exponent below 5.2, scab seldom appears, but with exponents much above this figure the potatoes are generally scabbed.

W. G.

Chlorine Index as a Comparative Measure of the Richness of Soils in Humus. L. LAPICQUE and E. BARBÉ (*Compt. rend.*, 1919, **168**, 118—121).—The authors find that the amount of an aqueous solution of sodium hypochlorite decomposed in a given time by a given volume of soil varies considerably with the soil taken, and that this estimation forms a rough method of placing the soils in the order of their probable richness in humus, the volume of chlorine liberated varying directly with the humus content of the soil.
W. G.

Importance of Mould Action in the Soil. SELMAN A. WAKSMAN (*Soil Sci.*, 1918, **6**, 137—155).—Moulds have been isolated in large numbers from cultivated and uncultivated soil. By the growth of their mycelia, changes in the organic and inorganic constituents of the soil are brought about, but no nitrification or fixation of nitrogen is effected. Not much ammonia is produced in the presence of available carbohydrate as a source of energy, as it is absorbed in the formation of mould protein, but in the absence of carbohydrate considerable amounts of ammonia are left in the soil. Carbohydrates are decomposed with the formation of carbon dioxide. Moulds exercise an unfavourable effect on soil fertility in that they compete with green plants for available nitrogen compounds. On the other hand, they exercise also a beneficial effect on account of their large production of enzymes and acids, which produce further changes in soil constituents favourable to the growth of green plants. [See *J. Soc. Chem. Ind.*, 1919, February.]
J. H. J.

Nitrogen Compounds in Rain and Snow. FRANK T. SHUTT and R. L. DORRANCE (*Trans. Roy. Soc. Canada*, 1917—1918, [iii], **11**, 63—72).—A series of analyses of snow and rain which have fallen in or near Ottawa during the years 1908—1917 is recorded. The analyses deal with the nitrogen compounds, and are expressed as parts of nitrogen per million as (i) free ammonia, (ii) albuminoid ammonia, (iii) nitrates and nitrites. The average of these for the ten years is 0.461 nitrogen as free ammonia, 0.138 as albuminoid ammonia, 0.277 as nitrite and nitrate. This corresponds with 6.583 lb. of nitrogen per acre. A further analysis of the results for the various months is also given, from which it is shown that snow is decidedly poorer in all forms of nitrogen compounds than rain (compare A., 1915, i, 636).
J. F. S.

Composition of the Waters of the Inter-Mountain Region. J. E. GREAVES and C. T. HIRST (*J. Ind. Eng. Chem.*, 1918, **10**, 1001—1004).—Analyses of a large number of river waters are recorded, the majority of which are used for irrigation purposes. Whilst some of the waters are free from objectionable constituents, others, although good at their source, were found to contain large quantities of alkali sulphates, etc., after flowing through a district rich in soluble salts. The effect of these saline waters on vegetation is discussed.
W. P. S.

Organic Chemistry.

Products of the Action of the Silent Electric Discharge on Acetylene. H. P. KAUFMANN (*Annalen*, 1918, **417**, 34—59).—

After giving a résumé of previous work on this subject, the author describes in detail his own apparatus, photographs of which are given. The essential part consists of two concentric glass tubes about 75 cm. long having a space of 5 mm. between their walls. The interior of the inner tube is silvered, and through it a rapid stream of cold water is passed. The outer tube is immersed in dilute sulphuric acid, in which is a cooling coil. Electrical connexion is made between the silvered surface and the sulphuric acid with the poles of an induction coil operated by a high-frequency machine (230—250 volts, 2·5—3 amperes). A stream of acetylene is passed between the tubes, and all air in the apparatus must be completely displaced by the acetylene before the silent discharge is passed. When the reaction vessel is allowed to get warm, the product is a mixture of a solid and a liquid, but if the vessel is kept cold, a liquid product only is obtained, which collects at the bottom of the vessel at the rate of about 30—50 grams per hour. The liquid is a brown, viscous oil having an unpleasant odour. It has the composition $(C_2H_2)_x$ and is very unstable, changing by warming, by keeping in solution, or by the attack of almost any chemical agent into the solid, which appears to be identical with that described by de Wilde (*Ber.*, 1874, **7**, 357). The liquid decomposes and carbonises above 100° , but a small quantity distils at $70^\circ/10$ mm., which is a mixture of several substances; the residue in the flask changes to a plastic mass, which ultimately becomes brittle.

The solid product obtained in the warm reaction vessel is more conveniently obtained by warming a solution of the liquid product in ether at about 60° . It is a pale yellow, odourless powder, which is insoluble in all solvents.

Both the liquid and the solid rapidly absorb oxygen, and it is only during such absorption that they produce any action on a photographic plate.

The solid does not react with a dilute solution of bromine under ordinary conditions, but is attacked by more concentrated solutions, hydrogen bromide being evolved. The liquid readily absorbs bromine, best in solution in carbon tetrachloride, a pale yellow powder being obtained, the composition of which appears to be $(C_2H_2Br)_{28}$, assuming it to be an individual substance.

A 98% alcoholic solution of silver nitrate produces with a solution of the liquid product in carbon tetrachloride a pale yellow, flocculent precipitate of a silver derivative, which explodes on heating; the presence of a $:CH$ group in the liquid product is thus indicated.

By boiling with 47% nitric acid, the solid product yields nitro-

compounds of high molecular weight, together with a little benzoic acid. By oxidation with alkaline permanganate, the liquid product yields benzoic, *isophthalic*, and *terephthalic* acids. The same three acids are obtained, although with much greater difficulty, by oxidising the solid product with alkaline permanganate. C. S.

Allyl Alcohol. M. J. STRITAR (*Monatsh.*, 1918, **39**, 617—626).—Bromine is quantitatively absorbed by allyl alcohol whether the former is in excess or not; the reaction is suitable for the exact quantitative estimation of allyl alcohol, which may be effected either by direct titration with bromine water until a permanent yellow coloration is obtained, or by treating the acidified aqueous solution of the alcohol with an excess of bromide-bromate solution, followed by addition of potassium iodide and titration of the liberated iodine with sodium thiosulphate (compare Stritar and Zeidler, A., 1904, ii, 686).

When bromination is effected in dilute aqueous solution, about 47·5% of the added bromine is immediately and spontaneously eliminated as hydrogen bromide. Elimination of the second bromine atom (exchange for hydroxyl) occurs slowly and incompletely in acid solution, small amounts of acraldehyde being formed. Practically the whole of the bromine is removed when the product is heated under pressure at 100° with the calculated quantity of potassium hydroxide (or with a 10% excess); the yield of glycerol is about 97% of that theoretically possible. The small deficiency is caused by the formation of a volatile, saturated bromide which is fairly resistant to alkali. H. W.

The System Ethyl Ether-Chloroform. A. SMITS and V. S. F. BERCKMANS (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 401—404).—A melting-point curve for various mixtures of ethyl ether and chloroform has been determined. The curve shows that an equimolecular compound is formed (m. p. $-94\cdot4^{\circ}$), as was stated by Dolezalek and Schulze (A., 1913, ii, 108), but, in addition, two other compounds, (i) a compound made up of two molecules of chloroform and one molecule of ethyl ether (m. p. $-93\cdot3^{\circ}$), and (ii) one made up of two molecules of ethyl ether and one of chloroform. The latter compound does not melt, but dissociates at $-113\cdot8^{\circ}$ into the equimolecular compound and ethyl ether.

J. F. S.

Physical Constants of "Mustard Gas" [$\beta\beta'$ -Dichloroethyl Sulphide]. LEASON H. ADAMS and ERSKINE D. WILLIAMSON (*J. Washington Acad. Sci.*, 1919, **9**, 30—35).—The compressibility of $\beta\beta'$ -dichloroethyl sulphide has been determined over the pressure range 392—1713 megabars at $31\cdot5^{\circ}$ by the method previously described (this vol., ii, 98). The compressibility is represented by the equations $\Delta v/v_0 = 4\cdot24 \times 10^{-5}(P - P_0) - 6\cdot3 \times 10^{-5}(P - P_0)^2$ and $-\Delta v/v_0 = 0\cdot118(1 - e^{-0\cdot364 \times 10^{-3}(P - P_0)})$. Differentiating this, the relationship $-dv/dP = 49\cdot5e^{-0\cdot364 \times 10^{-3}P}$. The compressibility at

$P=0$ is 49.5×10^{-6} per megabar, and at 1000 megabars it is 34.4×10^{-6} per megabar. The freezing pressure and volume change were also determined at a few temperatures, and the following results obtained:

Temp.	Freezing pressure. Megabars.	$(V_2 - V_1 \text{ c.c.})$	$dP/dT.$
13.9	1	0.054	68
21.9	570	0.050	71
29.6	1110	—	—
31.4	1210	0.047	74
38.9	1800	0.042	77

The latent heat of fusion per gram is found to be 25 cal.

J. F. S.

The Liquid Crystals of Agaricic Acid. PAUL GAUBERT (*Compt. rend.*, 1919, **168**, 277—279).—Agaricic acid gives two types of liquid crystals, one belonging to the cubic system and the other being optically uniaxial and positive. The crystals are but slightly birefringent, and consequently the polychroism is feeble.

W. G.

Phytochemical Reductions. XV. The Conversion of Acetaldo into Optically Active β -Butylene Glycol by Yeast.

CARL NEUBERG and (MME.) ELISABETH KERB (*Biochem. Zeitsch.*, 1918, **92**, 96—110).—The reaction, $\text{OH} \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CHO} \rightarrow \text{OH} \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$, takes place in the presence of yeast both when actively fermenting sugar and when, also, sugar is not added. A dextrorotatory product was obtained. The β -butylene glycol was, amongst other methods, characterised by preparing the di- α -naphthylurethane derivative, m. p. 154° , by its treatment with α -naphthylcarbimide.

A method is given for preparing in good yield acetaldo by the action of disodium sulphite on aldehyde in the cold (at -15°). From the aldol were prepared the β -bromophenylhydrazone, $\text{C}_{10}\text{H}_{13}\text{ON}_2\text{Br}$, white, seemingly hexagonal leaflets, m. p. 127 — 128° , and also the diphenylmethanedimethyldihydrazone,



colourless plates, m. p. 117° .

S. B. S.

Phytochemical Reductions. XVI. The Conversion of Citral into Geraniol by Yeast.

CARL NEUBERG and (MME.) ELISABETH KERB (*Biochem. Zeitsch.*, 1918, **92**, 111—123).—This reaction takes place both in the presence and absence of added sugar. The geraniol which is produced is accompanied by some optically active substance which has not yet been identified. The authors describe the two following derivatives of cyclocitral: the thiosemicarbazone, $\text{C}_{11}\text{H}_{19}\text{N}_3\text{S}$, white leaflets, m. p. 200 — 201° , and the p-nitrophenylhydrazone, $\text{C}_{16}\text{H}_{21}\text{O}_2\text{N}_3$, orange crystals, m. p. 125° .

S. B. S.

Preparation of Soluble Starch. A. LEULIER (*J. Pharm. Chim.*, 1918, [vii], **18**, 291).—Twenty-five grams of starch are boiled for fifteen minutes under a reflux apparatus with a mixture of 100 grams of 95% alcohol and 5 grams of sulphuric acid; the starch is then collected on a filter and washed with water or alcohol until free from acidity. Starch thus treated is insoluble in cold water, but very soluble in hot water. [See, further, *J. Soc. Chem. Ind.*, 1919, 86A.] W. P. S.

The Preparation of Methylamine from Chloropicrin. PERCY FARADAY FRANKLAND, FREDERICK CHALLENGER, and NOEL ALBERT NICHOLLS (*T.*, 1919, **115**, 159—162).

The Present Condition of the Benzene Problem. HERMANN PAULY (*J. pr. Chem.*, 1918, [ii], **98**, 106—135).—The various representations suggested for the benzene molecule are discussed. From a consideration of the relationships between the physical constants of benzene derivatives, the corresponding hydrogenated compounds, etc., the following conclusions are drawn: (1) The atoms of the benzene molecule lie in one plane. (2) The benzene ring must be symmetrically arranged and the linkings uniform. (3) Neither centric nor olefinic linkings are present, the degree of saturation of the linkings being approximately midway between those of simple and double linkings. Thiele's formula, the valence-electronic representation of benzene, the tetrahedral model, and the problem of orientation are also considered. T. H. P.

II-10-Bromophenanthrene-3- or -6-sulphonic Acid. HÅKAN SANDQVIST (*Annalen*, 1918, **417**, 1—16).—A hot aqueous solution of potassium phenanthrene-3-sulphonate is cooled to about 50° until crystals begin to separate, and a solution of bromine in water saturated at the ordinary temperature (about 3 mols. of bromine) is added gradually, whereby is obtained, in addition to oxidation products, potassium II-10-bromophenanthrene-3- or -6-sulphonate. The crude salt is converted through the chloride into II-10-bromophenanthrene-3- or -6-sulphonic acid, $C_{14}H_8Br \cdot SO_3H \cdot 4H_2O$, an almost white, non-crystalline mass, m. p. 152—153°, or, anhydrous, 223° (in a closed capillary, m. p. 160—170°), which has an astringent but, unlike the I-isomeride (*A.*, 1917, i, 552), no sweet taste, forms yellow, flocculent solutions, and shows some tendency to form liquid crystals. The *potassium, ammonium, sodium, calcium, barium, and copper* salts are described. The *methyl* ester, flattened needles, has m. p. 158°, the *ethyl* ester, needles, has m. p. usually 143·5°, but sometimes 134° (to a turbid liquid); the former yields methyl phenanthraquinone-3-sulphonate by oxidation with chromic and acetic acids. II-10-Bromophenanthrene-3- or -6-sulphonyl chloride, prepared from the potassium salt, forms faintly yellow prisms, m. p. 199—199·5°, from which are prepared the *amide*, $C_{14}H_{10}O_2NBrS$, needles, m. p. 266·5°, and the *anilide*, needles or leaflets, m. p. 211°. C. S.

I-10-Chlorophenanthrene-3- or -6-sulphonic Acid and 10-Chlorophenanthrene. HÅKAN SANDQVIST (*Annalen*, 1918, 417, 17—33).—It has been shown (A., 1917, i, 552) that the abnormal viscosity and anisotropy of solutions of I-10-bromophenanthrene-3- or -6-sulphonic acid disappear when the bromine is replaced by the $\cdot\text{SO}_3\text{H}$ or $\cdot\text{C}_{14}\text{H}_7\cdot\text{Br}\cdot\text{SO}_3\text{Me}$ group. It is now found that they are increased when the bromine is replaced by a chlorine atom.

I-10-*Chlorophenanthrene-3- or -6-sulphonic acid*, prepared by fusing together I-10-bromophenanthrene-3- or -6-sulphonyl chloride and phosphorus pentachloride, and heating the resulting chloride with water at about 145° , forms a white, microcrystalline powder possessing an acid, sweet, astringent taste. A 0.04*N*-solution has a viscosity 1.03 at 18° (water at $18^\circ=1$); this is increased to about 140 by the addition of one-sixth volume of 3*N*-hydrochloric acid, the value for I-10-bromophenanthrene-3- or -6-sulphonic acid being increased only to about 6 by similar treatment. The air-dried acid, m. p. $160\text{--}161^\circ$, contains $3\text{H}_2\text{O}$ (decomp.); the anhydrous acid has m. p. $206\text{--}207^\circ$. The *ammonium*, *sodium*, *potassium*, *calcium*, *barium*, and *copper* salts are described. The *methyl* ester, leaflets or prisms, has m. p. $172\text{--}172.5^\circ$, and the *ethyl* ester, colourless crystals, m. p. $182.5\text{--}183^\circ$. The *chloride*, $\text{C}_{14}\text{H}_8\text{Cl}\cdot\text{SO}_2\text{Cl}$, prepared as above, forms prisms, m. p. $196\text{--}197^\circ$, and from it have been obtained the *amide*, needles, m. p. $281\text{--}282^\circ$, and *anilide*, crystals, m. p. $197\text{--}198^\circ$.

10-*Chlorophenanthrene*, $\text{C}_{14}\text{H}_9\text{Cl}$, m. p. $35\text{--}55^\circ$ (purest specimen, $52.5\text{--}53.5^\circ$), b. p. $343\text{--}346^\circ$, is obtained, together with other products (of which 9:10-dichloroanthracene and 9:10-phenanthrene dichloride have been identified), by adding a cold solution of chlorine (26 grams) in carbon disulphide to phenanthrene (50 grams) dissolved in the same solvent. It yields phenanthraquinone by oxidation, forms a *picrate*, $\text{C}_{14}\text{H}_9\text{Cl}\cdot\text{C}_6\text{H}_5(\text{NO}_2)_3\cdot\text{OH}$, yellowish-red needles, m. p. $111\text{--}112^\circ$, and is converted by sulphonation at $165\text{--}170^\circ$ into a sulphonic acid, from which the preceding I-10-chlorophenanthrene-3- or -6-sulphonyl chloride, m. p. $196\text{--}197^\circ$, can be prepared. C. S.

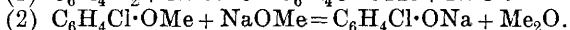
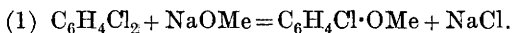
The Mobility of the Methylnitroamino-group in the Derivatives of Tetranitrophenylmethylnitroamine and in Trinitrodi(methylnitroamino)benzene. C. F. VAN DUIN (*Rec. trav. chim.*, 1919, 38, 89—100).—A study of the action of ammonia, aniline, and *m*-nitroaniline on certain derivatives of 2 : 3 : 4 : 6-tetranitrophenylmethylnitroamine obtained by substituting the nitro-group in position 3 by an hydroxyl, an anilino-, a methylnitroamino-, an amino-, and a dimethylamino-group. The results show that a negative substituent in this position hinders the substitution of the methylnitroamino-group, whilst a positive substituent increases its mobility. As opposed to this, however, is the fact that in 2:4:6-trinitro-3-dimethylaminophenyl-

methylnitroamine, the methylnitroamino-group is not replaced by *m*-nitroaniline.

In the action of ammonia on 2:4:6-trinitro-1:3-di(methylnitroamino)benzene, two *compounds*, one having *m. p.* 195—196° (*corr.*) and the other having *m. p.* 144° (*corr.*), were obtained, but could not be characterised.

W. G.

The Formation of Phenol in the Action of Sodium Methoxide on the Higher Chlorobenzenes. P. W. DE LANGE (*Rec. trav. chim.*, 1919, **38**, 101—105. Compare Holleman and Mooy, A., 1916, i, 22).—The author finds that *p*-chloroanisole and *p*-dichlorobenzene when heated in sealed tubes at 176—177° with sodium methoxide in methyl alcohol each yielded *p*-chlorophenol and methyl ether, the reaction being far more complete with the *p*-chloroanisole than with the dichlorobenzene. He considers that the reaction with dichlorobenzene takes place in two stages, as follows:



W. G.

Velocity of Nitration of Phenols in Ethereal Solution. II. ALFONS KLEMENC and ELISABETH EKL (*Monatsh.*, 1918, **39**, 641—696. Compare A., 1914, i, 272).—The velocity constants of the nitration of phenol, guaiacol, *o*- and *p*-cresol, and resorcinol methyl ether have been determined. Nitration is, in general, found to be a positive autocatalytic process, and the rate of nitration is dependent on the proportion of nitrogen peroxide or nitrous acid in the nitric acid. From this point of view, a mathematical expression for the velocity of nitration of a benzene derivative has been developed which, when applied to the particular case of phenols, takes into account the fact that the nitrous acid formed during the course of nitration (the cause of the autocatalytic nature of the process) is itself absorbed by the phenol.

Pure nitric acid, free from nitrogen peroxide and nitrous acid, does not cause nitration. Nitrogen peroxide induces both the nitrating and oxidising action of nitric acid towards derivatives of benzene.

In the case of nitration in ethereal solution, action either does not occur at all or rapidly comes to an end if the number of molecules of nitric acid is greater than that of the phenol or guaiacol, this behaviour being, apparently, opposed to the law of mass action.

The necessary solutions are obtained by dissolving anhydrous nitric acid in dry ether at a temperature of −80° (solutions prepared in this manner remain colourless at 0° for weeks), and by dissolving nitrogen peroxide in the same solvent in a special form of apparatus, which is figured in the text and allows the necessary adjustment of concentration and removal of known amounts of solution. The course of the reaction is followed by

determining the decrease in the titre of the nitric acid at given intervals. In the case of phenol, this can be done directly with standard barium hydroxide solution (the nitrophenol behaving as indicator) during the early stages of the reaction; during the later stages, the end-point is obscured by coloured bye-products, and it is then preferable to shake the ethereal solution with saturated potassium chloride solution and to add potassium hydroxide or barium hydroxide until the nitric acid is neutralised, when the next drop extracts a portion of the nitrophenol from the ether and colours the aqueous solution deep red. In the cases of guaiacol and other phenols, this method cannot be used, and recourse must be had to the iodometric process previously described (*loc. cit.*).

In addition to the phenols already mentioned, experiments with catechol, resorcinol, and quinol are also described. In the first two cases, satisfactory results could not be obtained; with quinol, the initial reaction consisted in the evolution of nitric oxide and formation of quinhedrone, which gradually underwent nitration. It is noteworthy that the presence of nitrogen peroxide is here found to be essential to the oxidising action of the nitric acid.

H. W.

Oxidation of Quinol and its Sulphonic Acids by means of Fehling's Solution. JOH. PINNOW (*J. pr. Chem.*, 1918, [ii], 98, 81—95. Compare A., 1911, i, 339).—Further experiments show that, when oxidised by Fehling's solution in absence of air, quinol and its sulphonic acids require almost exactly 3 atoms of oxygen per molecule, and give dihydroxyquinol or its sulphonic acids. The less amount of Fehling's solution earlier found sufficient with low concentrations of quinol (compare Bourquelot and Fichtenholz, A., 1910, i, 273) is explained by concurrent oxidation at the expense of atmospheric oxygen. In presence of sulphite, quinol and its sulphonic acids are oxidised by means of Fehling's solution principally to dihydroxyquinoldisulphonic acid, 5 or 4 atoms, respectively, of oxygen being used; this oxidation proceeds by way of quinone, quinolsulphonic acid, quinonesulphonic acid, and quinoldisulphonic acid, and not by way of dihydroxyquinone and its sulphonic acids. Unlike quinone and its sulphonic acids, dihydroxyquinone and its sulphonic acids do not unite with sulphite. Part of the quinol, which is not oxidised by Fehling's solution to the readily separable dihydroxyquinonedisulphonate, yields a readily soluble, pale-coloured isomeride, but the most important side reaction is the action of the alkali on the quinone-sulphonate, which should lead through hydroxyquinolsulphonate to the final product of oxidation, hydroxyquinonesulphonate.

T. H. P.

Some Derivatives of Resorcinol. H. VERMEULEN (*Rec. trav. chim.*, 1919, 38, 106—111).—2-Nitroresorcinol when added to nitric acid (D 1.5) in the cold yields 2:4-dinitroresorcinol, m. p. 146°, which when converted into its potassium salt and heated with an excess of methyl sulphate gives 2:4-dinitro-1:3-dimethoxy-

benzene; this, when reduced with tin and hydrochloric acid in alcoholic solution and the product treated with acetic anhydride, gives 2-nitro-4-acetylamino-1:3-dimethoxybenzene, m. p. 161—162°. This compound on nitration yields 2:6-dinitro-4-acetylamino-1:3-dimethoxybenzene, m. p. 129°, which when hydrolysed gives 2:6-dinitro-4-amino-1:3-dimethoxybenzene, m. p. 141°. 4-Acetylamino-1:3-dimethoxybenzene, m. p. 117°, when nitrated in acetic acid solution yields 6-nitro-4-acetylamino-1:3-dimethoxybenzene, m. p. 173°, which is also obtained by the acetylation of 6-nitro-4-amino-1:3-dimethoxybenzene, m. p. 136—137°, obtained by the reduction of 4:6-dinitro-1:3-dimethoxybenzene. W. G.

Acetylsalicylic [*o*-Acetoxybenzoic] Acid. HENRY L. DAHM (*J. Ind. Eng. Chem.*, 1919, **11**, 29—30).—The melting point of aspirin is determined by immersion of the capillary tube in a stirred paraffin oil bath heated at the rate of 1° per minute, the thermometer being immersed during the whole time of heating, but the melting-point tube inserted only when the temperature reaches 130°. The free salicylic acid present may be determined by comparison of the colour given with dilute ferric chloride with a series of cobalt chloride solutions of various concentrations. [See *J. Soc. Chem. Ind.*, 1919.] T. H. P.

The Elimination of the Carbethoxyl Group from Tautomeric Systems. I. Derivatives of Indene. CHRISTOPHER KELK INGOLD and JOCELYN FIELD THORPE (*T.*, 1919, **115**, 143—159).

Preparation of Mercury Derivatives of Phthaleins and Analogous Compounds. SACCHARINFABRIK AKT.-GES. VORM. FAHLBERG, LIST, & Co. (D.R.-P. 308335; from *Chem. Zentr.*, 1918, ii, 881—882).—Neutral solutions of the alkali salts of phthaleins, succineins, and "sacchareins" are boiled with large excess of a mercuric salt, particularly mercuric chloride, whereby uniform products are formed in an easily isolable condition. Thus, fluorescein and mercuric chloride yield a reddish-brown product, insoluble or sparingly soluble in the usual organic media, soluble in sodium carbonate, sodium hydroxide, or ammonia, to deep red solutions, which show a strong, greenish-yellow fluorescence when diluted. The ammoniacal solution is blackened by ammonium sulphide at its boiling point. The sodium salt of methylfluorescein gives a pale brown derivative with mercuric chloride which dyes silk orange-yellow. Mercuriated compounds from dibromofluorescein, tetrabromofluorescein, tetraiodofluorescein, phenolphthalein, tetraiodophenolphthalein, quinolphthalein, hydroxyquinolphthalein, resorcinsuccinein, cresorcinsuccinein, and resorcinsaccharein are also described. H. W.

The Reduction of Aromatic Ketones. W. D. COHEN (*Rec. trav. chim.*, 1919, **38**, 72—88).—In acid solution, benzophenone is reduced with the formation of benzopinacolone, benzhydrol not being formed. If the action is energetic, a little diphenylmethane is

formed. In an alkaline medium, on the other hand, benzhydrol is almost exclusively obtained unless the alkali is very weak, in which case a little benzopinacone is formed. An energetic reduction produces some diphenylmethane. In neutral medium, as when reduced by aluminium amalgam in alcohol, benzophenone yields 68% of benzhydrol and 32% of benzopinacone.

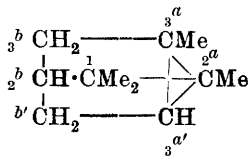
W. G.

Preparation of β -Anthrimides. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 308666; from *Chem. Zentr.*, 1918, ii, 882).—The products of the action of ammonia on β -diazanthraquinones are heated in solvents of high boiling point with or without a condensing agent. Thus, anthraquinone- β -diazonium sulphate is made into a paste with alcohol and treated with well-cooled, concentrated alcoholic ammonia; the product is heated with nitrobenzene under reflux, when $\beta\beta'$ -dianthrimide separates as a dark brownish-red substance, which becomes yellowish-brown when dried or acidified; it forms a scarlet solution in concentrated sulphuric acid, which gradually becomes olive and then green. The product from 1:3-dibromoanthraquinone- β -diazonium sulphate and alcoholic ammonia gives *tetrabromo- β -dianthrimide* (partly as the benzoyl derivative, which is hydrolysed with concentrated sulphuric acid) when heated to gentle boiling with nitrobenzene and benzoyl chloride. The substance is yellow and yields a bluish-green solution in concentrated sulphuric acid; it dyes cotton yellow from a reddish-brown bath. *Dichlorobisdiazanthraquinoneamide* (from diazotised 1-chloro-2-aminoanthraquinone and ammonia in excess) is pale yellow, and is converted by treatment with boiling nitrobenzene and benzoyl chloride into 1:1'-*dichloro-2:2'-dianthrimide*, orange-yellow, matted needles soluble in concentrated sulphuric acid to a pure blue solution; it dyes cotton orange-yellow from a reddish-brown bath.

H. W.

***sec.*- β -Methylcamphor and *sec.*- β -Phenylcamphor, a New Series of Synthetic Camphors, and *tert.*-Naphthylborneol and Naphthylcamphene.** J. BREDT (*J. pr. Chem.*, 1918, [ii], 98, 96—105).—In consequence of the publication of Ruzicka's paper (*A.*, 1918, i, 398), the author gives a short account of work carried out in 1914—1918.

[With MARIA SAVELSBERG].—The action of magnesium methyl iodide on camphor or on fenchone yields the tertiary alcohols, methylborneol and methylfenchol, which, under the action of dehydrating agents, yield one and the same *hydrocarbon*, $C_{11}H_{18}$, b. p. 172—175°, m. p. 71—73°, which shows great stability towards permanganate, and is regarded as a homocyclene of the annexed structure. When treated with acetic and sulphuric acids, the hydrocarbon yields an *acetyl* compound, $C_{13}H_{22}O_2$, b. p. 106—107°/13 mm., and this on hydrolysis gives a secondary *alcohol*, $C_{11}H_{20}O$, m. p. 193°, which forms a *phenylurethane*, m. p. 102°; oxidation of the alcohol yields a



α^*

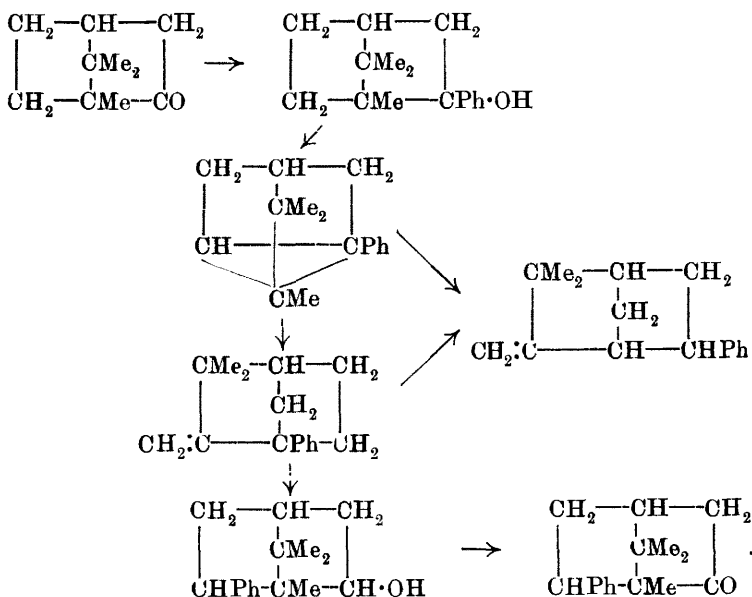
ketone (β -methylcamphor), $C_{11}H_{18}O$, m. p. 167—168°, giving an *oxime*, m. p. 125—127°, and a *semicarbazone*, m. p. 255° (decomp.), and yielding 2-methylcamphoric acid, $C_{11}H_{18}O_4$, m. p. 191°; the *anhydride* of the acid has m. p. 205·5—207°. The properties of these products indicate that they belong to the camphor series, so that, in the splitting of the trimethylene ring of the hydrocarbon (see formula above), the linking $3^a-3^{a'}$ is ruptured. This indication is confirmed by the molecular refraction of the *ethyl* ester of the acid; this ester has $D_4^{18.2}$ 1·0289, which differs but little from the value, D_4^{20} 1·0298, for ethyl camphorate, whereas ethyl *isofencho*-camphorate has D_4^{20} 1·0054. The specific exaltation of the molecular refraction of the ester of the new acid, $E\Sigma_D = -0.229$, is similar to that, -0.18 , for ethyl camphorate, and is conditioned by the annexed grouping, whilst in ethyl *isofencho*-

camphorate the grouping $\begin{array}{c} | \\ \text{CH}-\text{CH}_2-\text{C}-\text{Me} \\ | \\ \text{Me} \end{array}$ produces no exaltation. The following further derivatives of the 2-methylcamphoric acid were prepared: the *dichloride*, b. p. 155°/15 mm., the *chlorinated chloride*, the *chloro-anhydride*, m. p. 204—206°, the *sec.-tert.-amino-acid*, m. p. 162—163°, and its *calcium* salt, and the *acid imide*, m. p. 256°.

[With A. C. HEINEMANN and F. GOBLET.]—The interaction of magnesium phenyl bromide and camphor, followed by treatment of the product with water and dilute hydrochloric acid, yields the *tert.*-phenylborneol, m. p. 41°, b. p. 119·5—120·5°/2—2·5 mm., $[\alpha]_D^{20} - 50.33^\circ$ (in benzene), already prepared by Haller. Treatment of this tertiary alcohol with acetic anhydride gives a liquid *hydrocarbon*, $C_{16}H_{20}$, b. p. 99°/2 mm., D_4^{14} 0.9920, $[\alpha]_D^{19} + 3.27^\circ$, which is converted into the *acetyl* derivative of a tertiary alcohol, b. p. 136°/2 mm., m. p. 87°. This hydrocarbon partly undergoes rearrangement to an *isomeride*, b. p. 86°/2 mm., $D_4^{12.7}$ 1.0034, $[\alpha]_D^{18} - 3.75^\circ$, whilst a third *isomeride*, b. p. 106°/2 mm., m. p. 33—34.5°, $D_4^{29.6}$ 0.9742, is formed in good yield on repeated dry distillation of the above acetyl compound. The hydrocarbon, b. p. 99°/2 mm., does not combine with hydrogen chloride in light petroleum solution, but the isomeride, b. p. 86°, forms the *hydrochloride*, $C_{16}H_{21}Cl$, m. p. 76.5°, which with milk of lime gives a *tertiary alcohol*, $C_{16}H_{22}O$, b. p. 106.5°, $[\alpha]_D^{140} + 23.06^\circ$, isomeric with the *tert.*-phenylborneol. Hydrolysis of the above acetyl derivative yields a secondary *alcohol*, $C_{16}H_{22}O$, m. p. 115—116°, which, like the products derived from it, is optically inactive. Oxidation of this alcohol by means of chromic acid gives a *phenylcamphor*, $C_{16}H_{20}O$, m. p. 68°, the formation of which takes place as shown on p. i, 127.

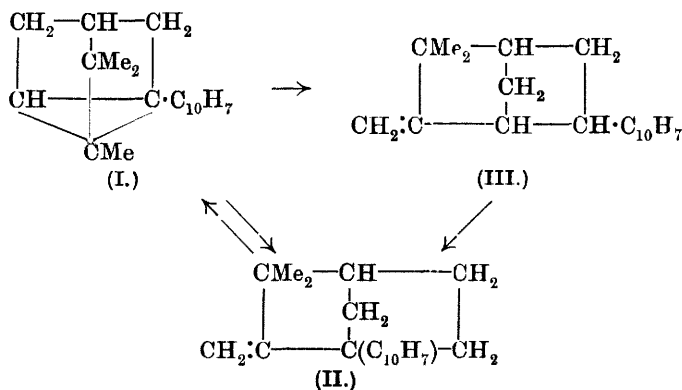
The new phenylcamphor forms a *semicarbazone*, m. p. 189—190°, and an *oxime*, m. p. 141—142.5°, and when reduced with sodium and alcohol gives a mixture of phenylborneol and phenylisborneol, which were not separated. With sodiopotassamide and amyl nitrite, phenylcamphor yields the *isonitroso*-derivative, which forms

greenish-white crystals, m. p. 189° , and this with sodium hydrogen sulphite gives *phenylcamphorquinone*, a golden-yellow substance, m. p. 145° . The latter is also obtained by the action of permanganate on *phenylcamphorcarboxylic acid*, m. p. $149-150^{\circ}$ (evolu-



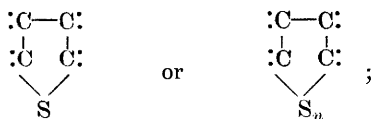
tion of CO_2), which is formed from phenylcamphor with the help of sodiopotassamide and carbon dioxide. *Phenylcamphoric acid*, $\text{C}_{16}\text{H}_{20}\text{O}_4$, m. p. 123.5° , is formed by the protracted action of permanganate solution on the quinone; its *anhydride*, $\text{C}_{16}\text{H}_{18}\text{O}$, m. p. 173.5° , was prepared.

[With H. DUSSIER.]—The action of magnesium α -naphthyl bromide on camphor yields *tert.-naphthylborneol*, m. p. $122-124^{\circ}$,

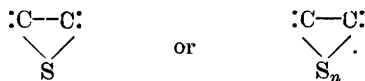


$[\alpha]_D^{15} - 41.96^\circ$ in benzene. When subjected to dry distillation, this alcohol yields the *naphthylcamphene*, $C_{20}H_{22}$, which crystallises in felted needles, m. p. $92-93^\circ$, b. p. $210^\circ/16$ mm., and gives no hydrochloride with dry hydrogen chloride in ethereal solution. Treatment of the hydrocarbon with acetic and sulphuric acids yields only an *isomeride*, m. p. $116-117^\circ$. From results obtained with methylcyclohexene and phenylcamphene, it may be assumed that the naphthylcamphene, m. p. $92-93^\circ$, has structure I or II, and that treatment with acetic and sulphuric acids, under the influence of the naphthyl residue, leads to rearrangement to the compound III, which cannot be acetylated. T. H. P.

Condensation of Unsaturated Compounds in Relation to Terpenes, Resins, and Caoutchouc. H. J. PRINS (*Chem. Weekblad*, 1919, **16**, 64—74).—The type of condensation discussed is that between molecules of the same substance containing the group $:C=C:$. The reaction is brought about by catalysts, such as acids, acid anhydrides, halogens and halogen compounds with active halogen, sulphur and sulphur compounds (persulphides), oxygen and peroxides, metallic oxides, and metals. The catalyst and substrate are "reciprocally activated." Three reactions are possible: polymerisation of the unsaturated substance, combination of catalyst with the substance at the double bond, and combination of catalyst with the polymerised substance formed. The theory of reciprocal activation is discussed in relation to the simultaneous polymerisation and oxidation of unsaturated hydrocarbons, such as terpenes, the formation of resins, and the vulcanisation of caoutchouc. The following theory for the last-mentioned process is suggested. The caoutchouc molecule is rendered active by means of the catalyst sulphur, whilst the sulphur undergoes a change analogous to the formation of ozone from oxygen in presence of unsaturated substances. There results (1) a simple polymerisation of the caoutchouc molecule with formation of *cyclobutane* derivatives; (2) polymerisation of the caoutchouc molecule with inclusion of sulphur in the ring, giving compounds of the type



(3) direct addition of sulphur at the double bond to form :



W. S. M.

Constituents of Resins. III. Further Investigation of Siaresinol from Siamese Gum Benzoin. ALOIS ZINKE and HANS LIEB (*Monatsh.*, 1918, **39**, 627—639).—It has been previously shown that the benzoresinol obtained by Lüdy from

Sumatra gum benzoin (A., 1893, i, 480—666) is probably a mixture of *d*-sumaresinol and *l*-benzoresinol (A., 1918, i, 502); further examination of the substance prepared according to Lüdy's directions only led to the isolation of siaresinol (A., 1918, i, 398). Lüdy's benzoresinol should therefore be deleted from the literature.

Further examination of *d*-sumaresinol and siaresinol has shown that these substances are acidic in character, and that the acidic hydrogen is contained in the carboxyl, and not in the hydroxyl group as assumed by Lüdy (*loc. cit.*); the former is therefore to be regarded as *d*-sumaresinolic acid and the latter as *d*-siaresinolic acid. Oxidation of *d*-siaresinolic acid leads to the formation of a monobasic acid, $C_{27}H_{40}O_4$, and the loss of three atoms of carbon and eight atoms of hydrogen appears to denote the elimination of a propyl or an isopropyl group; the formula for the parent substance may be written $C_3H_7 \cdot C_{26}H_{40}O_2 \cdot CO_2H$.

[With LUDWIG ZECHNER.]—*Silver siaresinolate* forms a white powder which darkens in colour when preserved, and decomposes when warmed with water, acetone, or alcohol. It is converted by methyl iodide into *methyl siaresinolate*, which crystallises in prismatic crystals with $1\frac{1}{2}H_2O$ from aqueous alcohol, m. p. about 150° , in needles with $\frac{1}{2}H_2O$ from benzene, and in anhydrous, prismatic crystals, m. p. 169 — 170° , from light petroleum. The *ethyl* ester separates from light petroleum in needles or prismatic platelets, m. p. 108° ; from aqueous alcohol in nodular masses, which melt indefinitely at 102° and contain water of crystallisation. The mixed *anhydride* of acetic and siaresinolic acids melts at 125 — 127° after softening at 104° .

Chromic acid oxidises the double compound of acetic and *d*-siaresinolic acid to an acid, $C_{27}H_{40}O_4$, short prisms, m. p. 317° , $[\alpha]_D^{16} -193\cdot8^\circ$ in chloroform solution; the *potassium* salt, long, white needles with $3\frac{1}{2}H_2O$, and the *methyl* ester, colourless leaflets, m. p. 186 — 187° , are described. H. W.

Hydroxymethylfurfuraldehyde. J. A. MIDDENDORP (*Rec. trav. chim.*, 1919, **38**, 1—71).—The author finds that ω -hydroxymethylfurfuraldehyde, obtained by the action of acids on the hexoses, can be distilled unchanged in an absolute vacuum, giving a distillate, b. p. 114 — $116^\circ/1$ mm., which will crystallise and has m. p. $31\cdot5^\circ$, $D_4^{15} 1\cdot268$, $D_4^{26} 1\cdot2629$, $n_D^{26} 1\cdot556$, $n_a^{24} 1\cdot552$, $n_b^{29} 1\cdot563$, and its heat of combustion is $664\cdot8$ cal. per gram-mol. Contrary to the general statements, the author finds that this aldehyde is miscible with water in all proportions, and that there is no indication of the formation of a hydrate. It gives a *phenylmethylhydrazone*, m. p. 161° , and an *aldazine*, m. p. 168° (decomp.), and its hydroxyl group may readily be replaced by halogen by the action of the hydrogen halide in dry ether. ω -Chloromethylfurfuraldehyde is readily converted into ω -methoxymethylfurfuraldehyde, an oil, b. p. 68 — $70^\circ/2$ mm., $D^{17\cdot9} 1\cdot146$, $n_D^{19\cdot6} 1\cdot5088$ giving a *phenylhydrazone*, m. p. 56 — 57° , a *p*-nitrophenylhydr-

azone, m. p. 140—141°, an *oxime*, an *aldazine*, m. p. 86°, a *semicarbazone*, m. p. 170°, and a *semioxamazone*, m. p. 209—210°. Similarly, *o*-ethoxymethylfurfuraldehyde gives a *p*-nitrophenylhydrazone, m. p. 140—141°, an *oxime*, an *aldazine*, m. p. 70°, and a *semioxamazone*, m. p. 212—213°. Benzoyloxymethylfurfuraldehyde gives a *phenylhydrazone*, m. p. 112°, a *p*-nitrophenylhydrazone, m. p. 142°, an *oxime*, m. p. 85—85.5°, an *aldazine*, m. p. 163°, a *semicarbazone*, m. p. 198°, and a *semioxamazone*, m. p. 204° (decomp.).

When distilled at a pressure of 10—20 mm., hydroxymethylfurfuraldehyde is partly decomposed, giving its anhydride, difurfurylmethyl ether, which yields a *semicarbazone*, m. p. 255°, and when oxidised by moist silver oxide gives di(2-methyl-5-carboxylfuryl) ether, m. p. 165°.

Sodium hydroxide readily decomposes hydroxymethylfurfuraldehyde, giving 2:5-dihydroxymethylfuran, m. p. 80°, and 5-hydroxymethylpyromucic acid. Under similar conditions, methoxymethylfurfuraldehyde gives 2-hydroxymethyl-5-methoxymethylfuran, b. p. 132—134°/23 mm., m. p. 37°, n_D^{15} 1.4860, and 5-methoxymethylpyromucic acid, m. p. 66—66.5°; the ethoxy-aldehyde similarly gives 2-hydroxymethyl-5-ethoxymethylfuran, b. p. 152—157°/20 mm., n_D^{15} 1.4865, and 5-ethoxymethylpyromucic acid, m. p. 62°.

Hydroxymethylfurfuraldehyde condenses with ethyl malonate, giving *ethyl hydroxymethylfurfurylidenemalonate*, m. p. 48.5°, b. p. 221°/11 mm., D_4^{20} 1.1648, n_D^{20} 1.539, n_D^{25} 1.536, and with malonic acid, giving *hydroxymethylfurfurylidenemalonic acid*, decomposing at 130°.

Ammonia or potassium cyanide react readily in alcoholic solution with hydroxy-, methoxy-, or ethoxy-methylfurfuraldehyde, but the products in every case resinify.

From a study of the absorption spectra of the coloured products obtained from furfuraldehyde and its methyl and hydroxymethyl derivatives, respectively, with the following reagents, resorcinol, Sesamé oil, β -naphthol, acetone, diphenylamine, egg-albumin, aniline acetate, narcotine, and orcinol, it is shown that the coloured products formed by warming sucrose with hydrochloric acid and the respective reagents resemble those obtained from hydroxymethylfurfuraldehyde, but differ from those obtained from furfuraldehyde itself. It is shown that diphenylamine is the most satisfactory reagent for distinguishing between pentoses and hexoses, and that the reaction with acetone is the most satisfactory for distinguishing methylpentoses from pentoses and hexoses. W. G.

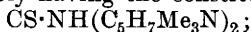
The Alkaloids of *Holarrhena congolensis*. FRANK LEE PYMAN (T., 1919, 115, 163—166).

Nicotine Content of the Smoke of Heavy, Light, and "Nicotine-free" Cigars. W. STORM VAN LEEUWEN (*Arch. exp. Path. Pharm.*, 1918, 84, 282—316).—This content was measured

physiologically by the effect on the blood-pressure of an acid extract of the smoke, and bears no relationship to the trade description or even to the nicotine content of the cigars themselves. The smoke of so-called nicotine-free cigars (Wendt) contains as much as that of average normal ones. A full account of earlier work is given.

G. B.

Cyclic Acetone Bases. C. HARRIES (*Annalen*, 1918, **417**, 107—191. Compare A., 1896, i, 317).—The author has shown that vinyl-diacetonamine-oxime (4-oximino-2:2:6-trimethylpiperidine) yields α -4-amino-2:2:6-trimethylpiperidine by reduction with zinc dust and cold alcoholic hydrochloric acid, and β -4-amino-2:2:6-trimethylpiperidine by reduction with sodium and boiling amyl alcohol (*loc. cit.*, and A., 1897, i, 293). These two bases behave differently towards carbon disulphide. Whilst the β -base yields only one dithiocarbamate which cannot be converted into a thiocarbimide by mercuric chloride, the α -base yields an easily soluble dithiocarbamate, which is changed by boiling water into a sparingly soluble dithiocarbamate; from the last, hot aqueous mercuric chloride solution produces a substance which has the composition of the expected thiocarbimide, but not its properties, and is therefore probably an internal thiocarbamide. By treatment with iodine, the two α -dithiocarbamates (2 mols.) lose carbon disulphide (1 mol.) and hydrogen sulphide (1 mol.) and yield two isomeric thiocarbamides, probably having the constitution



these are probably syn- and anti-stereoisomerides, and so also are the two α -dithiocarbamates.

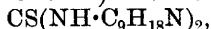
The question why the β -base does not yield an analogous series of isomerides cannot be answered at present.

[With A. BAUDREXEL, H. HOHENEMSER, and R. HAARMANN.]—Between 1896 and 1908, the reduction of 4-oximino-2:2:6-trimethylpiperidine to α -4-amino-2:2:6-trimethylpiperidine by cold alcoholic hydrogen chloride and zinc dust has frequently been effected. It is all the more remarkable, therefore, that the authors, using present-day zinc dust (since 1913), have obtained, not the above α -base, but 2:2:6-trimethyl-4-piperidone. In order to prepare the α -base, therefore, 4-oximino-2:2:6-trimethylpiperidine has been reduced by 3% sodium amalgam in 80% alcoholic solution at 10—20°, 25% hydrochloric acid being constantly added to maintain an acid reaction. This method produces about equal weights of α - and β -4-amino-2:2:6-trimethylpiperidine; the hydrochloride of the latter is insoluble in absolute alcohol.

[With BERNHARD SCHELLHORN.]—Whether reduced by cold alcoholic hydrochloric acid and zinc dust or by boiling amyl alcohol and sodium, 4-oximino-2:2:6:6-tetramethylpiperidine yields only one 4-amino-2:2:6:6-tetramethylpiperidine, leaflets, m. p. 16—18°, b. p. 79°/7 mm., which is converted by acetic anhydride into the acetate of the acetylamino-derivative, m. p. 205°; the acetylamino-

derivative itself, $C_{11}H_{22}ON_2$, forms pyramidal crystals, m. p. 120° , b. p. $161-163^\circ/6-8$ mm.

In cold ethereal solution, 4-amino-2:2:6:6-tetramethylpiperidine (2 mols.) and carbon disulphide (1 mol.) yield 4-amino-2:2:6:6-tetramethylpiperidine 2:2:6:6-tetramethylpiperidylthiocarbamate, $C_9H_{18}N \cdot NH \cdot CS \cdot SH, C_9H_{18}N \cdot NH_2$, crystals, m. p. 154° , but in the ratio of 1:1 yield tetramethylpiperidylthiocarbamic acid, $C_9H_{18}N \cdot NH \cdot CS \cdot SH$, m. p. 180° ; this, and also the preceding salt, are converted into a substance, m. p. 205° (decomp.), by recrystallisation from boiling water. The dithiocarbamic acid in boiling aqueous-alcoholic solution is converted by alcoholic iodine into the hydriodide (two crystalline forms) of the thiocarbamide,



triangular plates, m. p. 170° .

Corresponding with the production of two alkamines by the reduction of 2:2:6-trimethyl-4-piperidone (Harries, A., 1897, i, 293), it is found that 2:2-dimethyl-6-isobutyl-4-piperidone, reduced by sodium amalgam in faintly acid solution, yields a mixture of labile *cis-valerdiacetonalalkamine* [4-hydroxy-2:2-dimethyl-6-isobutylpiperidine], $NH < \underset{CMe_2}{\overset{CH(CH_2Pr^s) \cdot CH_2}{\text{---}}} CH_2 > CH \cdot OH$, m. p. $91-92^\circ$ (hydrochloride, m. p. 215°), and the stable *trans-isomeride*, m. p. 65° ; the former is converted into the latter by heating with a solution of sodium amyl oxide.

2:2-Dimethyl-6-isobutyl-4-piperidone forms an *oxime*, $C_{11}H_{22}ON_2$, needles, m. p. 121° (monohydrochloride, m. p. 238° ; dihydrochloride, needles, m. p. 222°), which is reduced by sodium and boiling amyl alcohol to 4-amino-2:2-dimethyl-6-isobutylpiperidine, $C_{11}H_{24}N_2$, b. p. $147^\circ/65$ mm. (hydrochloride, $C_{11}H_{24}N_2 \cdot 2HCl$; acetate of the acetyl derivative, m. p. $143-144^\circ$). The base yields a carbamate by absorption of carbon dioxide, and is converted by nitrous acid into the preceding *cis*-alkamine, m. p. $91-92^\circ$.

By warming with acetic anhydride, 2:2:6-trimethyl-4-piperidone is converted into its *acetyl* derivative, prisms, m. p. 92° , which yields *acetylvinylacetonalamineoxime* (1-acetyl-4-oximino-2:2:6-trimethylpiperidine), m. p. 130° , by treatment with aqueous hydroxylamine.

[With A. ZART.]—Benzylidenediacetonamineoxime yields only products of fissive decomposition when reduced by zinc dust and alcoholic hydrochloric acid, but is converted by reduction with sodium and boiling amyl alcohol into β -4-amino-2-phenyl-6:6-dimethylpiperidine, six-sided plates softening at 60° , no definite m. p., b. p. $183^\circ/36$ mm., which is isolated as the *hydrobromide*, $C_{13}H_{20}N_2 \cdot 2HBr$, prisms with $3H_2O$, m. p. 75° , decomp. 100° ; the *hydrochloride*, *platinichloride*, *hydriodide*, and *picrate* are mentioned.

[With AUGUST BAUDREXEL.]— α -4-Amino-2:2:6-trimethylpiperidine and ethyl chloroformate react in cold ether to form the *hydrochloride*, $C_{11}H_{22}O_2N_2 \cdot HCl$, crystals, m. p. $244-245^\circ$, of

α-ethyl trimethylpiperidylcarbamate, b. p. 148—150°/12 mm. (*picrate*, m. p. 208—209°). Attempts to eliminate ethyl alcohol from the carbamate with the object of creating a bridge linking in the 1:4-position were unsuccessfully made with zinc chloride, fused sodium acetate, phosphoric anhydride, phosphoryl chloride, and concentrated hydrochloric acid. The *α*-aminotrimethylpiperidine reacts in ethereal solution with carbon dioxide to form the *carbamate*, $C_5H_7Me_3N \cdot NH \cdot CO_2H, NH_2 \cdot C_5H_7Me_3N$, m. p. 112°.

The following compounds of the *β*-series were prepared by similar methods: *β-ethyl 2:2:6-trimethylpiperidyl-4-carbamate*, b. p. 151—152°/12 mm., m. p. 68°, and its *hydrochloride*, m. p. 253—254° (decomp.), and *picrate*, m. p. 164—165°; *β-aminotrimethylpiperidine trimethylpiperidylcarbamate*, m. p. 92°.

[With A. ZART.]—*α*- and *β*-4-Amino-2:2:6-trimethylpiperidine yield *dibenzoyl* derivatives, $C_{22}H_{26}O_2N_2$, m. p. 192—193° and 210—211° respectively, on benzoylation. The *α*-base reacts with phenylcarbimide in cold benzene to form the *phenyltrimethylpiperidylcarbamide*, $NHPh \cdot CO \cdot NH \cdot C_5H_7Me_3N$, needles, m. p. 211—212°, and with phenylthiocarbimide in ethereal solution to form the corresponding *thiocarbamide*, $C_{15}H_{23}N_3S$, crystals, m. p. 110°, whilst the hydrochloride of the *α*-base reacts with potassium cyanate in concentrated aqueous solution to form *α-trimethylpiperidylcarbamide*, $C_5H_7Me_3N \cdot NH \cdot CO \cdot NH_2$, leaflets, m. p. 55° (not sharp), decomp. below 100°. The corresponding substances in the *β*-series are *phenyltrimethylpiperidylcarbamide*, m. p. 130—138°, the *thiocarbamide*, $C_{15}H_{23}N_3S$, m. p. 160—161°, and *β-trimethylpiperidylcarbamide*, m. p. 170—171°.

[With HERBERT THOERL.]—Equal molecular quantities of 2:2:6-trimethyl-4-piperidone and ethyl chloroformate in ethereal solution, heated on the water-bath with a saturated solution of potassium carbonate, yield *ethyl 4-keto-2:2:6-trimethylpiperidine-1-carboxylate*, m. p. 34—35°, b. p. 141—142°/12 mm. (*oxime*, leaflets, m. p. 136°). The oxime is reduced by sodium amalgam and a mixture of alcohol, water, and acetic acid on the water-bath to *ethyl 4-amino-2:2:6-trimethylpiperidine-1-carboxylate*, b. p. 160°/12 mm., from which an internal 1:4-carbamide could not be produced.

The direct methylation of 2:2:6-trimethyl-4-piperidone at the imino-group is very difficultly effected. The result is attained indirectly, however, by oxidising *α*- and *β*-*N*-methylvinylidiacetonalkamines (see below) by chromic and acetic acids. Although the *α*-isomeride is very resistant to oxidation, both yield the same *N-methylvinylidiacetonamine* (1:2:2:6-tetramethyl-4-piperidone), b. p. 96—97°/14 mm., which is purified through the *hydrobromide*. It forms an *oxime*, prisms, m. p. 93° (*picrate*, needles, m. p. 216° [decomp.]).

[With AUGUST BAUDREXEL.]—The following derivatives have been prepared with the object of obtaining substances suitable for

the easy identification of the more important cyclic acetone bases, but none of them compares with the oxime for this purpose. 2:2:6-Trimethyl-4-piperidone forms a *semicarbazone*, $C_9H_{18}ON_4$, crystals, m. p. 196—197° (*oxalate*, m. p. 182°), the triacetoneamine forms a *semicarbazone*, $C_{10}H_{20}ON_4$, crystals, m. p. 219—220°, whilst benzylidenediacetoneamine forms a *p-nitrophenylhydrazone*,

$$C_{19}H_{22}O_2N_4,$$

m. p. 105—106°.

[With ARTHUR ZART.]—4-Hydroxy- α - and - β -1:2:2:6-tetramethylpiperidines are readily obtained by heating the 4-hydroxy-2:2:6-trimethylpiperidines with 40% formaldehyde on the water-bath. The hydrochloride of the α -compound reacts with benzoyl chloride at 120° to form α -4-benzoyl-1:2:2:6-tetramethylpiperidine, b. p. 194—195°/16 mm. (*hydrochloride*, m. p. 192°, *platinichloride*, m. p. 208° [decomp.], *nitrate*, and *picrate*, m. p. 180—181°). The corresponding β -benzoyl derivative has b. p. 195°/15 mm., and forms a *hydrochloride*, m. p. 58° (not sharp), *platinichloride*, m. p. 218° (decomp.), *nitrate*, m. p. 163° (decomp.), and *picrate*, m. p. 213°.

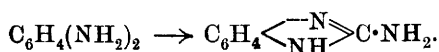
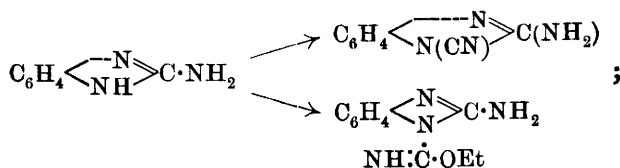
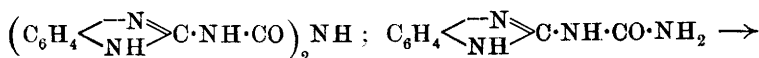
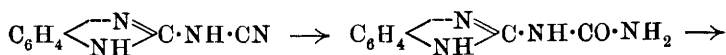
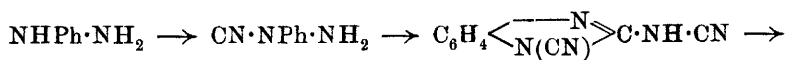
[With ERICH GROSCHUFF.]—The behaviour of cyclic acetone bases towards nitrous acid has been already published (A., 1901, i, 745).
 C. S.

New Mode of Formation of Pyrrole-black. A. ANGELI and A. PIERONI (*Atti R. Accad. Lincei*, 1918, [v], 27, ii, 300—304. Compare A., 1918, i, 547).—Treatment of pyrrole with the calculated quantity of magnesium ethyl iodide in very dilute ethereal solution, and passage through the liquid of a gentle current of air for about twenty-four hours, yields a voluminous, very black powder, which may be obtained almost free from ash by treatment with dilute sulphuric acid. This substance is far more intensely black than the pyrrole-blacks obtained by methods previously described, and, like these and the natural melanins, it does not melt, but furnishes vapours which turn a pine splinter moistened with hydrochloric acid an intense red; it is insoluble in all ordinary solvents, and also in alkali solutions. It is slowly oxidised by hydrogen peroxide in acetic acid, or dilute aqueous permanganate, or dichromate and dilute sulphuric acid. The compositions of the different pyrrole-blacks obtained in various ways are given. The yellowish-white product formed, together with pyrrole-black, by the action of peracetic acid, is probably a derivative of tripyrrole, and its composition is in agreement with the formula $C_{12}H_{17}O_3N_3$. Like aniline-blacks, pyrrole-blacks react readily with phenylhydrazine.

T. H. P.

Action of Cyanogen Haloids on Phenylhydrazine. IV. Passage to Derivatives of *o*-Phenylenediamine. G. PELLIZZARI and AUGUSTO GAITER (*Gazzetta*, 1918, 48, ii, 151—182).—Further

investigations (compare A., 1892, 1323; 1907, i, 873 and 1911, i, 338) show that it is possible to effect the following series of changes:



$\alpha\beta$ -Dicyano-*o*-phenyleneguanidine, $\text{C}_6\text{H}_4\left\langle\begin{array}{c} \text{---N---} \\ \text{N(CN)} \end{array}\right\rangle\text{C}\cdot\text{NH}\cdot\text{CN}$, obtained by the action of cyanogen bromide on α -cyanophenylhydrazine in presence of water and pieces of marble, forms white crystals, and turns yellow and then brown when heated, but does not melt at 300° ; it reacts acid towards litmus, and emits ammonia when heated with alkali hydroxide. The sodium salt forms a crystalline magma, and the potassium salt a gelatinous mass.

β -Cyano-*o*-phenyleneguanidine, $\text{C}_6\text{H}_4\left\langle\begin{array}{c} \text{---N---} \\ \text{NH} \end{array}\right\rangle\text{C}\cdot\text{NH}\cdot\text{CN}$, prepared by the action of potassium hydroxide on the preceding compound, forms long, thin, elastic, shining needles, and turns yellow at 240° and softens and decomposes at 250 – 260° ; it has slightly acid properties and exhibits normal ebullioscopic behaviour in alcohol. It is highly resistant to the action of potassium hydroxide, and only in a sealed tube at 140° is it possible to detach the β -cyanogen group. Its *silver* salt was prepared and analysed.

o-Phenylene- β -guanylcabamide, $\text{C}_6\text{H}_4\left\langle\begin{array}{c} \text{---N---} \\ \text{NH} \end{array}\right\rangle\text{C}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, obtained as hydrochloride by the action of hot dilute or cold concentrated hydrochloric acid, forms shining, colourless needles and becomes opaque, but does not melt at 300° . Its *hydrochloride*, $\text{C}_6\text{H}_4\text{ON}_4\cdot\text{HCl}$, decomposing at 255 – 260° , *platinichloride*, and *picrate* were prepared and analysed.

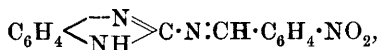
Diphenyleneguanylbiuret, $\left(\text{C}_6\text{H}_4\left\langle\begin{array}{c} \text{---N---} \\ \text{NH} \end{array}\right\rangle\text{C}\cdot\text{NH}\cdot\text{CO}\right)_2\text{NH}$, obtained by heating the preceding compound at 180 – 200° , crystallises in slender needles.

o-Phenyleneguanidine, prepared by the action of hydrochloric acid on *o*-phenyleneguanylcabamide or $\alpha\beta$ -dicyano-*o*-phenylene-

guanidine, is identical with the compound obtained from cyanogen bromide and *o*-phenylenediamine (compare Pierron, A., 1908, i, 926). The following salts were prepared and analysed: *carbonate*; *nitrate*, exploding without melting at 225°; *acetate*, m. p. 218°; *picrate*, m. p. 270° (decomp.); and *platinichloride*, + $\frac{1}{2}$ H₂O, which softens at 225°, and then melts and decomposes. The free base may be recognised by the alkaline reaction of its aqueous solution towards litmus and by the intense blue coloration, changing to green and then to brownish-yellow, obtained by the action of hypobromites or hypochlorites.

Acetyl-o-phenyleneguanidine, $\text{C}_6\text{H}_4\langle\text{N}^{\text{---}}\text{NH}\rangle\text{C}\cdot\text{NHAc}$, forms slender, white needles, m. p. 314—315° (decomp.). The action of nitrous acid on the corresponding benzoyl derivative (compare Pierron, *loc. cit.*) yields phenylenecarbamide, $\text{C}_6\text{H}_4\langle\text{N}^{\text{---}}\text{NH}\rangle\text{C}\cdot\text{OH}$ or $\text{C}_6\text{H}_4\langle\text{NH}\rangle\text{CO}$.

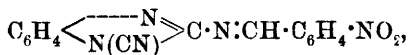
m-Nitrobenzylidenephenyleneguanidine,



prepared from *o*-phenyleneguanidine and *m*-nitrobenzaldehyde in presence of a drop of piperidine, forms minute, yellow needles, m. p. 170°.

α-Cyano-o-phenyleneguanidine, $\text{C}_6\text{H}_4\langle\text{N}^{\text{---}}\text{N(CN)}\rangle\text{C}\cdot\text{NH}_2$, obtained from *o*-phenyleneguanidine and cyanogen bromide, forms long, colourless needles, and decomposes at 173—175°, rapidly in a moist atmosphere and slowly in a desiccator. Its *platinichloride* turns brown at 100° and undergoes change when boiled with water.

m-Nitrobenzylidene-α-cyano-o-phenyleneguanidine,



prepared by the interaction of *α*-cyano-*o*-phenyleneguanidine and *m*-nitrobenzaldehyde in alcoholic solution in presence of a drop of piperidine, forms microscopic, yellow crystals and decomposes at 285—290°.

α-Ethoxy-o-phenylenecarbiminoguanidine, $\text{C}_6\text{H}_4\langle\text{N}^{\text{---}}\text{N}\rangle\text{C}\cdot\text{NH}_2$,
NH:Ċ·OEt

obtained together with the preceding compound, forms colourless needles, m. p. 155°. Its *platinichloride* forms pale yellow rhombs, m. p. 222—224° (decomp.). With *m*-nitrobenzaldehyde in presence of a drop of piperidine, the base yields *m-nitrobenzylidene-α-ethoxy-o-phenylenecarbiminoguanidine*, C₁₇H₁₅O₃N₅, which crystallises in pale yellow needles, m. p. 205—206° (decomp.).

According to Pierron (*loc. cit.*), the action of cyanogen bromide (3 mols.) and sodium hydrogen carbonate (3 mols.) on *o*-phenylene-

diamine (1 mol.) yields a little phenyleneguanidine and a large proportion (120—140% of the phenylenediamine used) of iminodiacarbonylphenyleneguanidine, C_6H_4 . This

compound may be obtained also from phenyleneguanidine (1 mol.), cyanogen bromide (2 mols.), and sodium hydrogen carbonate (2 mols.), or from phenyleneguanidine and biuret. The mechanism of its formation is under investigation. T. H. P.

Simultaneous Biochemical Syntheses of Gentiobiose and of the two β -Glucosides of Glycol by Emulsin. EM. BOURQUELOT and M. BRIDEL (*Compt. rend.*, 1919, **168**, 253—256). —From the products of the action of emulsin from almonds on a mixture of dextrose and ethylene glycol, in the molecular proportion of 2:1, in aqueous solution, the authors have isolated and characterised gentiobiose, glycylic β -glucoside, and glycylic β -diglucoside. W. G.

Physiological Chemistry.

The Blood Sugar. GUSTAV KROK (*Biochem. Zeitsch.*, 1918, **92**, 84—89).—An analysis of the sugar in blood was made by Bang's micro-method, both before and after hydrolysis by acids in the case of rabbits, after ingestion of starch and of maltose (at varying intervals), and after administration of adrenaline, and a few similar analyses were made on the blood of the human subject. There was no appreciable difference in the reducing power before and after hydrolysis in any case, and the results give no support to Lépine's conception of the "sucre virtuel" of blood. S. B. S.

The Theory of Clotting. ALFRED PERUTZ and MAX ROSEMAN (*Biochem. Zeitsch.*, 1918, **92**, 90—95).—The amount of fibrin which is obtained by mixing serum and plasma stands in some proportional relationship to the amounts of these two components used, when they are employed in great dilutions. If diminishing amounts of serum are added to the same amount of plasma, the amount of fibrin formed diminishes. In the same way, diminishing amounts of plasma added to the same amount of serum also produce diminishing amounts of fibrin. If very great dilutions are employed of plasma and serum, so as to be near the limits of a reaction, in order that the reaction should take place at all, the serum concentration must be greater than the plasma concentration. S. B. S.

The Presence of Phosphates in Human Blood-serum. VII. JOH. FEIGL (*Biochem. Zeitsch.*, 1918, **92**, 1—83).—The author gives a very extensive and detailed review of the methods of separating the constituents which contain phosphorus in the blood, especially the lipid phosphorus and inorganic (acid soluble) phosphorus, giving in particular a detailed criticism of the recent methods of Bloor, Greenwald, and their collaborators. He also gives a critical account of the micro-methods for estimating the phosphorus after ashing, including the various nephelometric and colorimetric methods. He gives, finally, a series of tables of analyses of the phosphorus of the blood (chiefly lecithin phosphorus) in pathological cases obtained by himself by the employment of various methods. S. B. S.

Shark and Ray Liver Oils. M. TSUJIMOTO (*J. Chem. Ind., Tokyo*, 1918, **21**, 1015—1042).—The analytical values of the liver oils of thirteen species of Japanese sharks and five species of Japanese rays are given. The oil derived from the shark *Pristiurus pilosus* had an exceptionally high iodine value (309.0) and a very low sp. gr. (D_4^{25} 0.8664). It was found that all the shark liver oils of low sp. gr. (below 0.9) contained the hydrocarbon squalene, which was also present in the egg oils of two species of shark, but it was not a constituent of any of the ray liver oils. [See also *J. Soc. Chem. Ind.*, 1919, 109A.] C. A. M.

Genesis of Thiocyanic Acid in Animals. V. SERAFINO DEZANI (*Arch. Farm. sper. sci. aff.*, 1918, **25**, 278—288; from *Chem. Zentr.*, 1918, ii, 836—837).—The quantity of thiocyanic acid formed in the dog depends on the albumin content of the food; this result is in striking contrast with the experience of Brüylants and Grober with the human subject.

After administration of acetonitrile, thiocyanic acid could be detected in the blood serum and saliva of the dog as soon as in the urine; its formation cannot therefore in any case be an exclusive function of the kidneys. H. W.

Calcium—Form of Reserve in the Female of the Phasmides; its Forms of Elimination in the two Sexes. J. PANTEL (*Compt. rend.*, 1919, **168**, 242—244).—Calcium exists as a reserve in the form of its carbonate in the lower malpighian tubes of the females of the Phasmides. In both sexes, the principal form in which it is eliminated is as its phosphate, accessory forms being the oxalate and probably the urate. W. G.

Catalytic Action of Serpent Venoms on the Nucleic Acids. C. DELEZENNE and H. MOREL (*Compt. rend.*, 1919, **168**, 244—246).—Both plant and animal nucleic acids are hydrolysed by venoms from members of the Colubrids and Viperides groups. The curves showing the velocity of the reaction indicate that the reaction is catalytic, and it has been shown that the amount of

hydrolysis is independent of the amount of venom used. The optimum temperature is 50—52°, and the venom loses its hydrolytic powers if heated for a few minutes at 100° or if to the medium is added specific antivenom serum. The different venoms vary in the intensity of their catalytic action, this variation being in the same direction as is that of their toxicity. W. G.

The Guttameter and its Application to the Study of Drugs and Poisons. FRIEDRICH ESCHBAUM (*Ber. Deut. pharm. Ges.*, 1918, 28, 397—416).—The guttameter is a capillary pipette with a wide delivery orifice from which ten drops are collected in a weighing bottle and the weight recorded. The instrument is standardised with water at 20°, ten drops of which should weigh 1·20 grams. The weight of ten drops of the liquid, corrected by the factor of standardisation of the instrument, is proportional to the surface tension; thus the results are inversely proportional to those obtained with the stalagmometer. The author has extended certain observations of Traube and others on the use of this instrument, from which it was deduced that the toxicity of solutions of alkaloids is in direct relation to the lowering of the surface tension of water produced by the alkaloid at standard concentration. Thus a number of derivatives of the quinine alkaloids have been studied and ranged in the order of decrease in surface tension produced in 0·1% solutions of their salts mixed with increasing small proportions of sodium carbonate. The order of classification so obtained coincides with that of increasing toxicity. Quinine and quinidine, approximately equal, had the least effect on surface tension; stronger depressions were recorded in the following order: hydroquinine, ethylhydrocupreine, ethylapohydroquinidine, *iso*-amylhydrocupreine, and *isooctyl*hydrocupreine. The depression of the surface tension increases with the amount of alkali added. Morphine and *apomorphine* occupy a peculiar position among the alkaloids in that solutions of their salts, when treated with sodium carbonate, do not show a depression of the surface tension as compared with water. It is shown, however, that morphine salts when treated with certain small proportions of ammonia liberate the alkaloid in a disperse form, and a depression of the surface tension is then observed. J. F. B.

Chemistry of Vegetable Physiology and Agriculture.

Action of Stimulants on Nitrifying Bacteria. C. MONTANARI (*Staz. sper. agr. ital.*, 1917, **50**, 69—72; from *Chem. Zentr.*, 1918, ii, 854. Compare A., 1914, i, 1159).—The action of compounds of copper, barium, lead, zinc, and arsenic has been investigated in extension of the work on manganese salts. The addition produces

different effects according as it takes place at the commencement of the experiment or when development of the nitrate ferment has occurred. In the former case, the formation of nitrates is hindered by small amounts of copper or by larger quantities of the other substances, whilst in the latter case the ferment is damaged by large doses of arsenic or, to some extent, of copper. Nitrification was not rendered more vigorous by minimal doses of the different substances, except in the solitary instance of manganese sulphate.

H. W.

The Chemistry of the Higher Fungi. XIII. *Scleroderma vulgare*, Fr., and *Polysaccum crassipes*, D.C. JULIUS ZELLNER (*Monatsh.*, 1918, **39**, 603—615. Compare A., 1915, i, 1086; 1918, i, 54).—Extraction of *Scleroderma vulgare*, Fr., with light petroleum yielded a deep brown, viscous mass containing an ergosterol and a resin. The ethereal extract contained fumaric acid, and further quantities of an ergosterol, which was not isolated in the pure state. Mannitol, dextrose, choline, and an amorphous carbohydrate were isolated from the alcoholic extract. Viscosin and potassium phosphate were isolated from the aqueous extract, in which neither invertases nor diastases could be detected.

Polysaccum crassipes, D.C., was similarly successively extracted with (1) light petroleum, (2) ether, (3) alcohol, and (4) water. The first extract was a dark brown, viscous mass rich in unsaponifiable matter, consisting of ergosterols and a reddish-brown resin. The second extract consisted of ergosterols; the presence of fumaric acid could not be definitely established. The third extract yielded dextrose, choline, and the *potassium ammonium* salt of a tannin-like acid (the free acid and its *silver* and *copper* salts are described), which probably has a glucosidic structure. The fourth extract contained a carbohydrate similar to that obtained from *Scleroderma*, together with mineral matter; the presence of ferments (invertase, maltase, diastase) could not be established.

H. W.

The Researches of Willstätter on the Assimilation of Carbon Dioxide. H. I. WATERMAN (*Chem. Weekblad*, 1918, **15**, 1138—1146).—A critical summary of the more recent work of Willstätter on the mechanism of the absorption and decomposition of carbon dioxide by chlorophyll.

W. S. M.

Action of Vegetable Enzymes on certain Organic Compounds. G. CIAMICIAN and C. RAVENNA (*Atti R. Accad. Lincei*, 1918, [v], **27**, ii, 293—300).—Much of this paper has been already published, the results not included in the previous abstract (this vol., i, 58) being briefly as follows.

Benzoic acid is not changed by the enzymes of pulped spinach leaves, but salicylic acid is largely oxidised; the respective sodium salts behave similarly. Coumarin remains unaltered, but mandelic acid is converted by spinach in an atmosphere of oxygen into a

compound which is not extracted by ether, but is reconverted into the original acid by boiling dilute sulphuric acid; in carbon dioxide, mandelic acid remains unaffected. Just as by the action of light, oxalic acid is almost completely oxidised by the enzymes, whilst succinic acid, which in the light is oxidised to a slight extent to glyoxal, acetaldehyde, acetic, and perhaps propionic acid, with the spinach enzymes yields acetaldehyde and a compound giving succinic acid when treated with emulsin. Lactic acid, which forms acetaldehyde and acetic acid on auto-oxidation in the light, yields only acetaldehyde under the action of the spinach. Malic acid, which gives formaldehyde, acetaldehyde, formic and acetic acids, and certain undefined products under the influence of light, yields only acetaldehyde with these enzymes.

Acetone is oxidised, as by light, to acetic and formic acids and formaldehyde, whilst methyl ethyl ketone gives propionic and formic acids under the influence of the spinach, its behaviour in light being unknown. The action of light on cyclic ketones results in hydrolysis to the corresponding aliphatic acids, and also in the formation of the corresponding dibasic or ketonic acids, whereas the action of the spinach enzymes converts these ketones into lower aliphatic acids and sometimes into succinic acid, the acids corresponding with the ketones used being never obtained. Thus, *cyclohexanone* gives formic acid and a mixture of volatile acids, apparently propionic and butyric. 2-Methyl*cyclohexanone* and 3-methyl*cyclohexanone* yield propionic and formic acids, and 4-methyl*cyclohexanone*, acetic acid, in addition. Menthone gives succinic, formic, acetic, and probably propionic acids. Pyridine, piperidine, nicotine, strychnine, and caffeine are not affected by the spinach enzymes, but morphine, quinine, and cinchonine undergo oxidation to a considerable extent.

Some of the compounds, such as benzoic acid, pyridine, piperidine, and nicotine, which resist attack by the enzymes of spinach, disappear when they are injected into maize and tobacco plants (*loc. cit.*). In one experiment, in which a total of 36 grams of sodium benzoate, corresponding with 30.5 grams of benzoic acid, were inoculated into twenty-five maize plants, 21.6 grams of the acid were afterwards found to have disappeared, and the plants yielded a distillate containing formic, acetic, and propionic acids in amounts corresponding approximately with the benzoic acid attacked.

T. H. P.

Biochemical Changes due to Environment. OTTO ROSENHEIM (*Biochem. J.*, 1918, **12**, 283—289).—The inflorescence of edelweiss (*Leontopodium alpinum*) contains a chromogenic substance, probably a flavone, which is not in glucosidic combination. It is best extracted with 90% alcohol at 70—75°. A comparative estimation of the amount present in plants grown in London at an altitude of 80 m. and in plants collected in the Alps at an altitude of 2000 m. shows the ratio of amounts present to be roughly as

1:4, and in addition the plants grown in the Alps contained traces of the chromogenic substance in glucosidic combination. These results show the biochemical adaptation of Alpine plants to changed environment, and support Shibata's hypothesis that the biological significance of flavones in the plant consists in their protective action against the injurious influence of ultra-violet light.

W. G.

'Essential Oil and Wax of Shuei Flower (*Jasminum odoratissimum*). R. TSUCHIHASHI and S. TASAKI (*J. Chem. Ind., Tokyo*, 1918, **21**, 1117—1143).—Fresh flowers of Shuei (*Jasminum odoratissimum*), cultivated in Formosa and used for perfuming tea, yielded on extraction with light petroleum 0.277% of concrete essence, which on maceration with alcohol was separated into 0.116% of essential oil and 0.166% of flower wax. The oil contained approximately 6% of *d*-linalool, 6% *d*-linalool acetate, 6% benzyl alcohol, 1.6% benzyl acetate, methyl ester of anthranilic acid and indole (10%), and constituents of high boiling point (possibly sesquiterpene alcohol or diterpene alcohol) about 57%. [See also *J. Soc. Chem. Ind.*, 1919, 117A.] C. A. M.

The Absorbent Power of Dry or Moist Earth with respect to Chlorine Gas. DANIEL BERTHELOT and RENÉ TRANNOY (*Compt. rend.*, 1919, **168**, 121—123).—Dry sand absorbs chlorine badly, but a peaty soil or leaf mould has very marked absorbent properties for this gas. The absorptive power is markedly increased by moistening the soil with 10% of its weight of water. Any further addition of water only causes an increased absorption, due to the water added.

W. G.

Connection between Absorption and Coagulation and its Relation to the Inorganic Colloids of the Soil. III. A. DE DOMINICIS and P. CHIARIERI (*Staz. sper. agr. ital.*, 1917, **50**, 451—479; from *Chem. Zentr.*, 1918, ii, 854. Compare A., 1915, i, 859; 1916, i, 240).—The previous results, that the action of electrolytes on the unstable hydrosols causes a single process resulting in coagulation through absorption, are confirmed by a series of experiments with the metals of the alkaline earths. When particles and ions with opposite charges come into contact, mutual attraction occurs, resulting in neutralisation of the charges and formation of absorption compounds. Decrease in concentration consequently follows both in colloidal and ionic-molecular solution. The physico-chemical properties of the soil are invariably favourably influenced with regard to fruitfulness by this phenomenon.

H. W.

The Organic Phosphorus of Soil. R. S. POTTER and R. S. SNYDER (*Soil Sci.*, 1918, **6**, 321—332. Compare Potter and Benton, A., 1917, i, 76).—For the most part a reply to Gortner and Shaw (compare A., 1917, i, 376). The authors have prepared the curves for the hydrolysis of phytin and of nucleic acid by 5%

sulphuric acid at 100°, and show that both these reactions are of the first order. No definite conclusions could be drawn from the curves for the hydrolysis of the organic phosphorus of three soils, but the direction of the curves was such as to indicate that the organic phosphorus might have been due to phytin or to a pyrimidine nucleotide.

W. G.

The Presence of Aluminium as a Reason for the Difference in the Effect of so-called Acid Soil on Barley and Rye.

BURT L. HARTWELL and F. R. PEMBER (*Soil Sci.*, 1918, **6**, 259—279).—The authors find that although rye will grow far more satisfactorily on an acid soil than will barley, seedlings of both these crops are equally affected by a given amount of acidity, both in water and sand cultures. The authors attribute the different effect of the acid soil on the two crops to the presence of aluminium sulphate in the soil solution, and they show that equivalent amounts of aluminium sulphate and sulphuric acid when added to an optimum nutrient solution produce about the same depression on barley seedlings, and that whilst a similar depression of the rye crop is produced by the acid, the aluminium sulphate causes very little depression and scarcely affects the rye roots. Further, as the hydrogen-ion concentration of the nutrient solution containing the aluminium sulphate was only about one-fourth of that containing the acid, they conclude that aluminium exerts a toxic effect on the barley. This active aluminium may be largely removed from the soil solution by the application of lime or phosphates, even acid phosphates.

W. G.

Experiments with various Nitrogenous Fertilisers.

EILH. ALFRED MITSCHERLICH, S. VON SAUCKEN, and F. IFFLAND (*J. Landw.*, 1918, **66**, 187—198).—Sand cultures of oats were treated with one and the same fertiliser, composed of magnesium and potassium sulphates, sodium chloride, and calcium phosphate, the nitrogen in the different cultures of a series being supplied in the form of sodium nitrate, ammonium sulphate, "Kalkstickstoff," carbamide, and carbamide nitrate. The results show that carbamide and its nitrate are at least equivalent in manurial value to the old nitrogenous fertilisers. Owing to its ready solubility in water, carbamide nitrate should serve, without causing marked plasmolytic phenomena, and hence injuries to the plants, as an excellent top-dressing, and may certainly replace sodium nitrate for this purpose. The yields of straw and corn under the different treatments are given in the form of tables, and are also subjected to analysis.

T. H. P.

Influence of Two Different Nutriments on the Yield of Crops. EILH. ALFRED MITSCHERLICH (*Landw. Jahrb.*, 1918, **52**, 279—296; from *Chem. Zentr.*, 1918, ii, 854—856).—I. *Influence of two nutriments which are without mutual action.*—The effect of variation in the amounts of potassium and nitrogen on the growth

of oats has been investigated, use being made of potassium sulphate and ammonium nitrate. The factor of activity of the nitrogen is constant ($=1.14$) and independent of the amount of potassium; similarly, the factor of the potassium ($=2.48$) is constant and independent of the quantity of nitrogen. If the nutriment is present in an equally assimilable form (which may be assumed to be the case with salts which are soluble in water), and if they are not influenced by any external factor, it follows that, in order to secure an equal yield of oats, 2.18 times ($2.48/1.14$) as much nitrogen as potash must be supplied; potassium is better utilised than nitrogen by the plant.

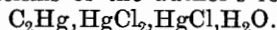
II. *Influence of two nutriments which react with one another.*
—Alterations in the increase in yield obtained by addition of either nutriment are immediately observed when the nutriment is either chemically or physically affected by other substances which are possibly introduced in the manuring, but which can be present in every possible combination in the soil in agricultural practice.
(a) *Chalk and phosphoric acid.*—Experiment shows that an equally good yield cannot be obtained by manuring with raw phosphate as with a readily soluble manure. Further, the maximum yield which can be obtained with a phosphate manure is diminished slightly at first, but more rapidly subsequently, by addition of chalk, and, finally, as is shown by experiments with phosphorite meal, to such an extent that an increase in yield due to the phosphate manure is scarcely noticeable. The value of different phosphate manures is affected in an extraordinary manner by the addition of chalk. Thus, the activity of tricalcium phosphate is diminished to considerably greater extent than that of a Thomas meal phosphate by addition of chalk; the value of the latter, however, does not remain constant, since a good specimen is found to be less affected than one of poorer quality. The relative value of tricalcium phosphate and Thomas meal T. in the absence of chalk is approximately the same as that previously found when calcium was added in large quantity in the form of calcium nitrate. Phosphatic manure loses much of its value if applied to land recently treated with chalk or marl or to soil rich in chalk unless other salts, such as ammonium sulphate, are also used. Manures which contain phosphates in a slightly soluble form are less effective in the presence of potash than those containing more soluble forms; raw phosphate is probably useless on land rich in chalk. It is doubtful if a preliminary manuring with phosphoric acid has any practical result. (b) *Potash and ammonium chloride.*—It has been previously found that the application of ammonium chloride, when sufficient nitrogen for nutriment is otherwise present, diminishes the value of manuring with potash; this result is now confirmed, and it appears to be not impossible that, under the given conditions, the ammonium chloride is physiologically acid, and therefore poisonous.
H. W.

Organic Chemistry.

The Influence of Catalysts on the Chlorination of Hydrocarbons. V. R. KOKATNUR (*J. Amer. Chem. Soc.*, 1919, **41**, 120—124).—Attempts were made to prepare pentachloroethane by the limited chlorination of *s*-tetrachloroethane. Various catalysts, such as vegetable and animal charcoal and metallic iron, were suspended in *s*-tetrachloroethane, and chlorine gas was passed through the liquid at various temperatures. In no case was pentachloroethane found among the products of the reaction, which consisted only of hexachloroethane and unchanged tetrachloroethane. In other trials, chlorination was effected by heating with bleaching powder and water and with anhydrous aluminium chloride. In these cases, also, hexachloroethane only was produced, although a certain amount of the tetrachloroethane was converted into *as*-tetrachloroethane. It is not decided whether this complete chlorination, giving hexachloroethane as the only product, is to be ascribed to the influence of catalysts or to the symmetrical structure of the tetrachloroethane, whereby both atoms of hydrogen are equivalent in function and are therefore substituted simultaneously. It is true that pentachloroethane may be produced by chlorinating in the presence of actinic light, but that may be due to the specific influence of the light on the constitution either of the *s*-tetrachloroethane, making it unsymmetrical, or of the chlorine molecule.

J. F. B.

Constitution of the Product of the Action of Acetylene on Mercuric Chloride. W. MANCHOT (*Annalen*, 1918, **417**, 93—106. Compare Manchot and Haas, A., 1913, i, 1009).—A reply to Biltz and Reinkober's criticisms of the author's formula,



[With FRANZ MÄHRLEIN.]—Styryl ethyl ether and an aqueous solution of mercuric acetate (3 mols.) are warmed at 50°, the cooled liquid is poured, after two hours, into a 10% solution of sodium chloride, whereby a white substance, $\text{CHPh}:\text{CH}\cdot\text{OH}, 2\text{HgCl}\cdot\text{OH}$, is obtained. It melts partly at about 120°, decomposes somewhat violently when heated over a free flame, is scarcely attacked by dilute sodium hydroxide solution, and yields phenylacetaldehyde by heating with hydrochloric acid.

In view of the preceding observations, the author now inclines to the opinion that the product of the action of acetylene on mercuric chloride, Biltz and Mumm's "trichloromercuriacetaldehyde," is an additive product of vinyl alcohol; a formula is not recorded, on account of the uncertainty of the individual character of the substance.

C. S.

Constitution of Geraniol, Linalool, and Nerol. ALBERT VERLEY (*Bull. Soc. chim.*, 1919, [iv], 25, 68—80).— α -Citral when boiled with 1% aqueous sodium hydroxide gives β -methyl- Δ^8 -heptenone, $\text{CH}_2\text{:CMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COMe}$, b. p. 168° , which when oxidised with potassium permanganate gives the glycol, $\text{HO}\cdot\text{CH}_2\cdot\text{CMe}(\text{OH})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COMe}$, which when oxidised with chromic acid only gives traces of acetone. β -Methyl- Δ^8 -heptenone when warmed on a water-bath with dilute sulphuric acid is readily transformed into its Δ^9 -isomeride, $\text{CMe}_2\text{:CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COMe}$ (compare Tiemann, *Ber.*, 1895, 28, 21, 2126). From these facts, the author assigns to geraniol, obtained by the reduction of citral, the constitution $\text{CH}_2\text{:CMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OH}$, which corresponds with citronellol. With hydrogen bromide, this geraniol gives a tribromo-compound,

$\text{CH}_3\cdot\text{CMeBr}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMeBr}\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$, which by treatment with alkali yields *isolinalool*, b. p. $200\text{--}207^\circ$, which thus has the constitution

$\text{CMe}_2\text{:CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}(\text{OH})\cdot\text{CH}\cdot\text{CH}_2$, ordinarily assigned to linalool, which must, therefore, be represented by the formula $\text{CH}_2\text{:CMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}(\text{OH})\cdot\text{CH}\cdot\text{CH}_2$. With hydrogen iodide, geraniol gives a monoiodo-derivative, which under the influence of alcoholic sodium hydroxide readily loses hydrogen iodide, giving a quantitative yield of nerol, to which the author assigns the constitution

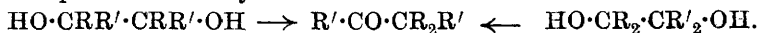
$\text{CMe}_2\text{:CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OH}$, previously attributed by Tiemann to geraniol. Nerol when oxidised with dilute chromic acid mixture gives *neral*, b. p. $120^\circ/20\text{ mm.}$, D 0.890, which is easily decomposed by alkalis, giving acetaldehyde and β -methylheptenone, and with an alkaline solution of cyanoacetic acid yields *nerylideneacyanoacetic acid*, m. p. 95° .

Of the substances of the geranic series occurring in nature, geraniol, citral, linalool, and methylheptenone, there exist two isomeric forms, α and β , of which the α -form is much the more abundant of the two, being accompanied by only a very small proportion of the β -form.

The new formula for geraniol given above permits of a ready explanation of the close relationship which exists between geraniol and dipentene, $\text{CH}_2\text{:CMe}\cdot\text{CH}\begin{matrix} \text{CH}_2\cdot\text{CH}_2 \\ \text{CH}_2\text{--CH} \end{matrix}\text{CMe}$. W. G.

Molecular Transpositions of α -Glycols. I. Introduction. A. ORÉKHOFF (*Bull. Soc. chim.*, 1919, [iv], 25, 9—19).—A theoretical discussion in which the author shows that Werner's theory (A., 1906, i, 436) combined with that of Tiffeneau (A., 1906, i, 724) can be successfully applied to the interpretation of the phenomena of the transpositions occurring in the dehydration of α -glycols. He attributes to each radicle an "aptitude for migration," or a "relative mobility" and a "saturation capacity" which vary with the different radicles, but in the same sense, and assumes that these control the transpositions, according to which he shows

that the symmetrical and asymmetrical isomeric glycols give the same products of dehydration:



These transpositions may, however, be modified by the nature of the dehydrating agent, and in the case where R or R' is a phenyl group by the introduction of substituents into the benzene nucleus. The benzyl group apparently has a smaller "mobility" and a smaller "capacity of saturation" than the phenyl group. W. G.

Preparation of Methyl Sulphate. WALTER NORMAN HAWORTH and JAMES COLQUHOUN IRVINE (Brit. Pat., 122498).—For the production of methyl sulphate, dimethyl ether and sulphur trioxide are caused to combine directly in the presence of a solvent. The sulphur trioxide may, if desired, be employed in the form of the dilute gas produced by the reaction of sulphur dioxide with air by the contact process. Both the sulphur trioxide and the methyl ether vapours must be perfectly dry, and the latter must be free from the vapours of alcohol. The two gases are passed simultaneously in approximately equimolecular proportions into the solvent liquid, which may conveniently consist of methyl sulphate itself. The mixture is stirred continuously and cooled by a water-jacket or coil. The methyl sulphate produced is drawn off and treated with iron filings or other reducing agent to neutralise the influence of any excess of sulphur trioxide which may be present; it is then purified by rectification under diminished pressure.

J. F. B.

Preparation of Acetic Acid from Acetylene. FARBEN-FABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 297442; from *Chem. Zentr.*, 1919, ii, 61).—Acetylene is treated with solutions of hydrogen peroxide, persulphuric acid or monopersulphuric acid, or solutions or suspensions of their salts in acids in the presence of mercury or mercury compounds. Thus a quantitative yield of acetic acid is obtained in a single operation when acetylene is treated with solutions or suspensions of persulphates in water or acids in the presence of mercury or mercury compounds. Salts of monopersulphuric acid, solutions of persulphuric acid and monopersulphuric acid, and of hydrogen peroxide may also be used; in place of the latter, any substance (percarbonates, peroxides) may be employed which yields hydrogen peroxide when acidified.

H. W.

Manufacture of Ethylidene Diacetate. SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE (Brit. Pat., 112765).—The reaction between acetylene and glacial acetic acid for the production of ethylidene diacetate is caused to take place in the presence of aromatic or aliphatic sulphonic acids and mercuric acetate, and in the absence of mineral acids or acid salts of mineral acids. The formation of tarry by-products and the secondary decomposition of the ethylidene diacetate are thereby suppressed. Suitable acids are benzene-

sulphonic, naphthalenesulphonic, camphorsulphonic, sulphoacetic, methionic acids, etc. Forty parts of mercuric oxide are dissolved in 200 of glacial acetic acid, a solution of 50 parts of β -naphthalenesulphonic acid in 200 of glacial acetic acid is added at 70°, and the mixture is caused to absorb 200 parts of acetylene during two hours at 70°. The excess of acetic acid is then separated from the ethylidene diacetate in the usual way. J. F. B.

Preparation of the Bromoisovaleric Ester of Bromoamylene Hydrate. EMIL RATH (D.R.-P. 309455; from *Chem. Zentr.*, 1919, ii, 61).—The ester is obtained as a pale yellow oil of faint, characteristic odour, which can be distilled in a vacuum by heating a molecular mixture of bromoamylene hydrate and bromoisovaleryl bromide in the presence of an indifferent solvent at the temperature of the water-bath until hydrogen bromide ceases to be evolved; bromoisovaleryl chloride may be used in place of the corresponding bromide. H. W.

Theory of Acids. O. HINSBERG (*J. pr. Chem.*, 1918, [ii], 98, 145—154).—Elaborating the conception of multiple valency centres (A., 1917, ii, 173, 461; 1918, ii, 106), the author endeavours to correlate the acid properties of ethyl acetoacetate, oxy-acids, acetylene, hydrogen cyanide, hydrogen sulphide, and the halogen acids. Acids are compounds which contain hydrogen bound either alone (HCl; H₂S) or with other elements (oxy-acids; ethyl acetoacetate; hydrogen cyanide) to an element of groups V—VII of the periodic table. The acidic hydrogen atom is linked to one atom by a principal valency and to other atoms by several subsidiary valencies, the effect of this competition of forces being to render the hydrogen atom mobile.

The mobility and loose binding of the hydrogen atom within the acid molecule may be regarded as the preliminary condition for dissociation into anion and cation. C. S.

Nitration of Sucrose : Sucrose Octanitrate. E. J. HOFFMAN and V. P. HAWSE (*J. Amer. Chem. Soc.*, 1919, 41, 235—247).—After removal of acid, the product of the nitration of sucrose by sulphuric and nitric acids in the cold forms a tough, viscous, semi-transparent, slightly hygroscopic mass, which can be pulverised to a sticky, white powder when hardened by cooling. When heated and allowed to cool, it begins to flow sluggishly at 40° and then gradually sets, until at 8° it becomes very hard and brittle. When acid-free, it is fairly stable, and may be kept without appreciable change for weeks at the ordinary temperature, but it decomposes when heated at comparatively low temperatures, this decomposition becoming more rapid after long heating; it is very sensitive to friction or impact. The mean nitrogen content of different preparations was 15%, the molecular weight in freezing acetic acid, benzene, or nitrobenzene, 428.9—565.2, and the specific rotation, using light from a frosted tungsten lamp filtered through 6% dichromate solution, $[\alpha]^{20} + 56.66^\circ$.

Sucrose octanitrate, $C_{12}H_{14}O_8(NO_3)_8$, obtained by evaporation of the alcoholic solution of the above product at the ordinary temperature, forms elongated, acicular crystals, probably of the monoclinic, but possibly of the orthorhombic, system [HERBERT INSLEY], m. p. $85\cdot5^\circ$, $[\alpha]^{20} + 56\cdot05^\circ$; it has the normal molecular weight in freezing nitrobenzene, and when heated gradually from 33° to 87° in a period of nearly two hours it shows no signs of decomposition. Photomicrographs of the crystals are given. Sucrose octanitrate may be estimated in explosive mixtures by means of its rotatory power and nitrogen content ($15\cdot95\%$). T. H. P.

Preparation of Soluble Starch. JAMES CRAIG SMALL (*J. Amer. Chem. Soc.*, 1919, **41**, 113—120).—Starch may be entirely converted into soluble starch, without the formation of erythro-dextrin or other cupric reducing products, by boiling with alcoholic hydrochloric acid under carefully regulated conditions. These conditions have been studied, and the method adopted by the author consists in suspending 20 grams of starch in 100 c.c. of 95% alcohol, adding 0.75 c.c. of strong hydrochloric acid (D 1.19), and boiling for exactly ten minutes with continuous agitation. The conversion is stopped by adding all at once the previously determined quantity of sodium hydrogen carbonate solution necessary to neutralise the acid. The soluble starch is then washed several times with alcohol by decantation, collected on a filter, and dried. The experiments performed in establishing the conditions of the above method of preparation showed that the amount of hydrolysis bears a direct ratio to the concentration of the hydrogen ion, but it would appear that in favourable circumstances the complete conversion into soluble starch constitutes a definite stage preliminary to further hydrolysis, and that maltose is not split off from the starch molecule as a direct consequence of this change. This supports the idea that soluble starch is a hydrated starch. From soluble starch onwards, the hydrolysis again appears to bear a direct ratio to the acid concentration. J. F. B.

Relations between the Viscosity of Cellulose Nitrate Solutions and the Nitration Process, with Special Reference to Wood Cellulose. G. LEYSIEFFER (*Koll. Chem. Beihefte*, 1918, **10**, 145—178).—The material employed was a chemically pure wood cellulose prepared from deal. It contained α -cellulose 80.4, β -cellulose 6.8, γ -cellulose 12.8%. The ash amounted to 0.20% and the fat to 0.44%. The nitration with a mixed acid of known composition was performed much in the usual manner; both cold and hot washing were employed. The drying was effected at 36 — 40° for twenty-two hours. The nitrogen content of the product was estimated by the Schulze-Tiemann method, and the nitrates were further characterised by solubility determinations in alcohol or ether-alcohol (2:1). The viscosity of the acetone solutions of the nitrates was determined by the Ost viscosimeter.

As the results of a large number of experiments, tables and

graphs of which are given, the following conclusions are drawn: (1) By the nitration of cellulose, the same value for the viscosity is always obtained provided all the factors which influence the internal friction (composition of the nitrating acid, temperature of the bath, duration of the nitration, proportion by weight of cellulose to acid, method of preparation and properties of the cellulose employed) are kept constant. (2) The greater the nitric acid content of a nitrating acid, the higher is the viscosity of the nitrated cellulose in acetone solution. If, however, the percentage content of nitric acid equals or exceeds that of the sulphuric acid, smaller values are found for the internal friction. This diminution is more marked in the case of dilute nitrating acids than of concentrated nitrating acids. Increasing the water content from 0% to about 11% causes an increase of the viscosity, only, however, if the nitric acid content is less than the sulphuric acid content; otherwise, and if the water content exceeds the above limit, smaller values are obtained for the viscosity. (3) Nitration at temperatures below 0° produces nitrates having high viscosity values. The higher the temperature of nitration, the smaller is the viscosity. (4) The viscosity values vary considerably in the case of nitrates which have been nitrated for only a short time (five to thirty minutes). They increase so long as the nitrogen content increases, but prolonged action of the nitrating acid results in a diminution of the viscosity. (5) A close connexion is found between the nitrogen content of a cellulose nitrate and the internal friction of its acetone solution; the higher the nitrogen content, the higher is the viscosity. (6) Acetone solutions of cellulose nitrates become more mobile with keeping, strongly viscous solutions more so than less viscous solutions. (7) The kind, method of preparation, and previous treatment of a cellulose are of great influence on the viscosity. A high content of γ -cellulose causes increased viscosity in the nitrate. Nitrates from cotton cellulose show higher viscosities than those from wood cellulose.

C. S.

The *n*-Butylarvlamines. III. Constitution of the Nitro-derivatives of *n*-Butyl-*p*-toluidine. JOSEPH REILLY and WILFRED JOHN HICKINBOTTOM (T., 1919, 115, 175—181).

Amino-acids. HENRY DRYSDALE DAKIN (*Biochem. J.*, 1918, 12, 290—317).—By using a new method of extraction, the author has isolated a new aminohydroxy-acid and a new peptide from the products of acid hydrolysis of caseinogen.

When caseinogen is hydrolysed with sulphuric acid, and the latter subsequently removed as barium sulphate, on submitting the neutral concentrated solution of amino-acids to continuous extraction with butyl alcohol, it is found that five fractions can be obtained, as follows: (1) Monoamino-acids, both aliphatic and aromatic, which, although insoluble in butyl alcohol, are extracted in the above process, but deposited as a cream-coloured granular powder in the extraction flask. (2) Proline, soluble in alcohol and extracted by

butyl alcohol. (3) Peptide anhydrides (diketopiperazines), extracted by butyl alcohol, but separated from (2) by their sparing solubility in alcohol or water. (4) Dicarboxylic acids, not extracted by butyl alcohol. (5) Diamino-acids, not extracted by butyl alcohol, but separable from (4) by phosphotungstic acid and other means. It is noteworthy that no indications of racemisation of the products during this process have been observed, and materially higher yields of many amino-acids were obtained than by existing methods. The fact that the monoamino-acids, which are essentially insoluble in all alcohols, are extracted by butyl alcohol under the above conditions, is due to the passage of a certain amount of water into the alcohol, since the extraction is very unsatisfactory if the aqueous solution of amino-acids contains an excess of salts, such as calcium chloride.

Using this method, the author found as an average of five determinations 8.0% proline from caseinogen, and from his specimen he prepared 1-prolylhydantoin, $\text{CH}_2 < \begin{smallmatrix} \text{CH}_2 \cdot \text{CH} \cdot \text{CO} \\ \text{CH}_2 \cdot \text{N} - \text{CO} \end{smallmatrix} > \text{NH}$, m. p. 165—167°, $[\alpha]_D^{20} -232^\circ$ to -238.5° , by passage through the uramido-acid.

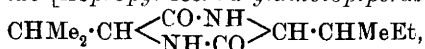
The method of extraction with butyl alcohol furnishes a ready means of obtaining a dry, almost neutral amino-acid mixture, which would serve as a basis for nutrient media with or without the addition of tryptophan, and might possibly find use for dietetic purposes, since most of the amino-acids which furnish dextrose in the diabetic organism are absent.

After the precipitation of the diamino-acids from the amino-acids not extracted by butyl alcohol, and subsequent separation of glutamic and aspartic acids, the former as its hydrochloride and the latter by the method of Levene and Van Slyke (compare A., 1910, i, 719), using freshly precipitated lead hydroxide, it was found that large amounts of at least one other dicarboxylic acid were still present, and it could be isolated. This acid, isolated through its silver salt, was characterised as β -hydroxyglutamic acid, $\text{CO}_2\text{H} \cdot \text{CH}(\text{NH}_2) \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, crystallising in stout prisms. It is optically active and extremely soluble in water. It yielded silver, copper, mercury, lead, cadmium, zinc, calcium, and barium salts, gave a diethyl ester, and on prolonged heating at 100—110° over phosphorus pentoxide lost a molecule of water,

giving a compound, $\text{CO} < \begin{smallmatrix} \text{NH} \cdot \text{CH} \cdot \text{CO}_2\text{H} \\ \text{CH}_2 \cdot \text{CH} \cdot \text{OH} \end{smallmatrix} >$. On heating the acid with zinc dust, an intense pyrrole reaction was obtained, and when reduced with fuming hydriodic acid at 150° it yielded glutamic acid, amongst other products. The sodium salt of the acid (1 mol.) when oxidised with chloramine-T (1 mol.) gave an aldehyde, $\text{C}_4\text{H}_6\text{O}_4$, which with *p*-nitrophenylhydrazine gave a characteristic osazone, $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{C}(\text{N} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2) \cdot \text{CH} \cdot \text{N} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$, m. p. 297—299°, giving a red ammonium salt. With potassium cyanate, β -hydroxyglutamic acid yielded a uramido-acid, which when heated with acids gave a very soluble hydantoin. The acid gave derivatives

with phenylcarbimide and β -naphthalenesulphonyl chloride, which were not well defined. It also gave characteristic colour reactions with various phenols and concentrated sulphuric acid.

The peptide mixture, extracted by the butyl alcohol from the products of hydrolysis of the caseinogen, was separated from proline, and obviously consisted of a number of different compounds. A tyrosine-containing peptide was isolated, but not identified, and also a peptide, which was shown to be d-isoleucyl-d-valine anhydride [isopropyl-sec-butyl diketopiperazine],



m. p. 310—312°, $[\alpha]_D^{20} - 42.0^\circ$ to -43.5° .

W. G.

Formation, by Oxidation, of Organic Substances, of an Intermediate Substance spontaneously producing Carbamide.

R. FOSSE (*Compt. rend.*, 1919, **168**, 320—322).—The author shows that whereas, by oxidation with potassium permanganate, substances such as casein and amino-acids give only a small yield of carbamide, if the oxidised solution is subsequently heated with aqueous ammonium chloride, a very much greater yield of carbamide is obtained. Similarly, if substances such as glycerol, carbohydrates, or formaldehyde are oxidised with potassium permanganate in the presence of ammonia, the yield of carbamide is practically negligible, but if the products are heated with aqueous ammonium chloride, a considerable yield of carbamide is obtained.

W. G.

The Action of Chlorine on Hydrazine, Hydroxylamine, and Carbamide. C. T. DOWELL (*J. Amer. Chem. Soc.*, 1919, **41**, 124—125).—When a large excess of chlorine is allowed to react with hydrazine and hydroxylamine in contact with carbon tetrachloride, evidence is obtained showing the formation of nitrogen trichloride, since on separating the carbon tetrachloride and treating it with a solution of potassium iodide, nitrogen is evolved. The author has confirmed the observations of Chattaway on the properties of dichlorocarbamide, in that when kept its solution is decomposed, giving as one of the products nitrogen trichloride. Chattaway considered that in the course of this decomposition carbon dioxide and monochloroamine were formed, the latter giving ammonia and nitrogen trichloride. The author, however, has tested the solution for monochloroamine by Raschig's test with ammonia and benzaldehyde, whereby, owing to the formation of hydrazine, the insoluble benzalazine should be produced. This is not the case, and no evidence of monochloroamine is obtained. It is suggested that the nitrogen trichloride may be formed by the action of chlorine, which may also be a decomposition product of dichlorocarbamide.

J. F. B.

Coal. AMÉ PICTET (*Ann. Chim.*, 1918, [ix], **10**, 249—330).—A more detailed account of work already published (compare A., 1911, i, 850; 1913, i, 1315; 1914, i, 155; 1915, i, 512; 1916, i, 800; 1917, i, 515).

W. G.

Halogenation. XVIII. Direct Iodination by means of Iodine and Nitric Acid. RASIK LAL DATTA and NIHAR RANJAN CHATTERJEE (*J. Amer. Chem. Soc.*, 1919, **41**, 292—295).—In continuation of the investigations on iodination by nitric acid (A., 1917, i, 332), it is found that the reaction takes place readily in the case of aromatic acids and aromatic haloid derivatives. Thus, iodobenzene gives a good yield of *p*-di-iodobenzene. Although a small proportion of trinitrophenol is formed as a result of the hydrolysis of iodobenzene and simultaneous nitration in presence of nitric acid (*loc. cit.*), it is not possible to prepare trinitrophenol catalytically by using a small quantity of iodine with continued addition of benzene and nitric acid, since iodobenzene is quite stable under these conditions, any excess of iodine yielding *p*-di-iodobenzene, and any excess of nitric acid, *p*-iodonitrobenzene. The latter is, however, formed by the prolonged action of iodine and nitric acid on benzene, since *p*-di-iodobenzene is decomposed by nitric acid, giving *p*-iodonitrobenzene, a good yield of which may be rapidly prepared by this method of exhaustive iodination of benzene with repeated additions of iodine and nitric acid; the water accumulating on account of the decomposition of nitric acid must be removed from time to time.

On iodination with the required quantity of iodine and nitric acid, iodobenzene gives *p*-di-iodobenzene; chlorobenzene gives *p*-chloriodobenzene, and bromobenzene, *p*-bromiodobenzene. *p*-Chloro- and *p*-bromo-toluenes give *p*-chloro- and *p*-bromo-benzoic acids respectively, the methyl groups being oxidised to carboxyl and no entry of iodine taking place. From benzoic acid, *m*-iodobenzoic acid was obtained, and from *o*-phthalic acid, 4-iodo-*o*-phthalic acid. Phenylacetic acid gives *p*-iodophenylacetic acid and cinnamic acid, *p*-iodocinnamic acid. Salicylic acid yields trinitrophenol quantitatively, the carboxyl group being detached, and complex hydroxy-acids, such as tannin, give a small quantity of trinitrophenol; the latter is frequently obtained in traces on iodination of the aromatic acids.

T. H. P.

Meta-substituted Aromatic Selenium Compounds. FRANK LEE PYMAN (T., 1919, **115**, 166—175).

Preparation of Monomethylaniline. PERCY FARADAY FRANKLAND, FREDERICK CHALLENGER, and NOEL ALBERT NICHOLLS (T., 1919, **115**, 198—205).

Preparation of "Metol" (*N*-Methyl-*p*-aminophenol Sulphate). ROLLA N. HARGER (*J. Amer. Chem. Soc.*, 1919, **41**, 270—276).—In view of the comparative cheapness of quinol and also of methylamine when prepared by the methylation of ammonium chloride by means of formaldehyde (compare Werner, T., 1917, **111**, 844; Jones and Wheatley, A., 1918, i, 527), the author has made experiments on the preparation of "metol" by heating quinol and methylamine together under pressure. The

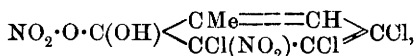
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results obtained show that a lower temperature, and consequently a very much lower pressure, and a much shorter period of heating than those given in the Merck specifications (A., 1913, i, 1057), are the conditions under which the reaction should be carried out; a yield of 73% is obtainable.

N-Methyl-*p*-aminophenol sulphate begins to char at 245° and has m. p. 250—260° (decomp.). It crystallises in microscopic, six-sided, prismatic needles with roof-like ends. Addition to its solution of mercuric acetate solution results in the gradual development of an intense purple coloration, which may probably serve for the colorimetric estimation of "metol." T. H. P.

Action of Nitric Acid on Halogen Derivatives of *o*-Alkylphenols. III. Nitric Acid Derivatives of Chlorinated *o*-Cresols. TH. ZINCKE and O. PREISS (*Annalen*, 1918, 417, 191—235. Compare Zincke and Pfaffendorf, A., 1912, i, 964; Zincke and Janney, A., 1913, i, 853).—The following new chloro-derivatives of *o*-cresol have been prepared. 4-Chloro-*o*-toluidine, by chlorination at 0° in glacial acetic and concentrated hydrochloric acids yields a *hexachloro-1-methylcyclohexene-2-one*, $C_7H_4OCl_6$, stout needles or prisms having a strong camphor-like odour, m. p. 105°, which is reduced in boiling alcoholic solution by tin alone to 3:4:5-trichloro-*o*-cresol, long needles, m. p. 77° (*acetyl* derivative, needles, m. p. 45°); if concentrated hydrochloric acid is also present, or if the reduction is effected by stannous chloride, tetrachloro-*o*-cresol is also produced. 3:5:6-Trichloro-*o*-cresol, needles, m. p. 62° (*benzoyl* derivative, needles, m. p. 110°), is prepared in a similar way from the keto-hexachloride obtained from 6-chloro-*o*-toluidine (Zincke and Pfaffendorf, *loc. cit.*). 4:5-Dichloro-*o*-cresol, needles, m. p. 101° (*benzoyl* derivative, needles, m. p. 80—81°), is obtained by leading the calculated quantity of chlorine into a chloroform solution of 4-chloro-*o*-cresol, needles, m. p. 73—74° (*benzoyl* derivative, leaflets, m. p. 53—54°), which is itself prepared from 4-chloro-*o*-toluidine.

3:4:5-Trichloro-*o*-cresolnitroquinitrol,

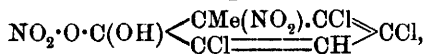


colourless, rhombic crystals, m. p. 105—106° (decomp.), obtained by adding 3:4:5-trichloro-*o*-cresol gradually to nitric acid, D 1.48, is converted into 3:4:6-trichloro-*p*-toluquinone by warm concentrated sulphuric acid, and is reduced (a) by stannous chloride, in cold dilute hydrochloric solution to 3:4:5-trichloro-*o*-cresol (a reduction of this kind cannot be effected with the corresponding tribromo-derivative, *loc. cit.*), (b) in methyl-alcoholic solution at 0° to 4:5-dichloro-3-nitro-*o*-cresol, yellow needles, m. p. 69° (*acetyl* derivative, rhombohedral crystals, m. p. 93—94°), and (c) in concentrated hydrochloric acid to 4:5-dichloro-3-amino-*o*-cresol, colourless leaflets, m. p. 161° (*hydrochloride*, leaflets; *diacetyl* derivative, needles, m. p. 194°; *triacetyl* derivative, leaflets, m. p. 126°), which is also obtained by the reduc-

tion of the preceding nitro-compound. The constitutions of these compounds are determined by the fact that the amino-compound can be converted into 4:5:6-trichloro-2:3-dihydroxytoluene.

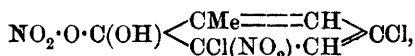
By boiling with tetrachloroethane, 3:4:5-trichloro-*o*-cresol-nitroquinitrol is converted into 4:5-dichloro-*o*-toluquinone 2-nitrate, $\text{NO}_2 \cdot \text{O} \cdot \text{C}(\text{OH}) < \begin{smallmatrix} \text{CMe} \cdot \text{CH} \\ \text{CO} - \text{CCl} \end{smallmatrix} > \text{CCl}$, yellow needles, m. p. 144° (decomp.), which is reduced by stannous chloride to 4:5-dichloro-2:3-dihydroxytoluene, needles, m. p. 107° (*diacetyl* derivative, needles, m. p. 112°). By chlorination in cold glacial acetic acid solution, 4:5-dichloro-2:3-dihydroxytoluene yields a *keto-chloride*, yellow prisms, m. p. 86—89°, which is reduced by stannous chloride to 4:5:6-trichloro-2:3-dihydroxytoluene. By oxidation with nitric acid (D 1·15) 4:5-dichloro-2:3-dihydroxytoluene yields 4:5-dichloro-2:3-toluquinone, dark red needles, m. p. 83°.

By treatment with nitric acid (D 1·48) 3:5:6-trichloro-*o*-cresol yields 3:5:6-trichloro-*o*-cresol-nitroquinitrol,

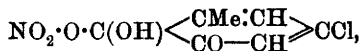


unstable, colourless crystals, m. p. 91° (decomp.). This differs from the 3:4:5-trichloro-isomeride in not being convertible into a dichlorotoluquinone nitrate, but resembles it in being converted into the trichlorotoluquinone by concentrated sulphuric acid. By boiling its solution in glacial acetic acid until nitrous fumes cease to be evolved and then reducing the cold solution with stannous chloride, 3:5:6-trichloro-*o*-cresol is regenerated. The nitroquinitrol is reduced by stannous chloride and dilute hydrochloric acid to 5:6-dichloro-3-amino-*o*-cresol, colourless needles (*hydrochloride*, needles; *diacetyl* derivative, needles, m. p. 204—205°), which is converted by chlorination in glacial acetic acid into a *keto-chloride* yielding 4:5:6-trichloro-2:3-dihydroxytoluene.

3:5-Dichloro-*o*-cresol-nitroquinitrol,



colourless needles, m. p. 109° (decomp.), obtained from 3:5-dichloro-*o*-cresol and nitric acid (D 1·48) is more stable than the two preceding nitroquinitrols, but it also decomposes slowly by keeping. It can be converted into 5-chloro-3-nitro-*o*-cresol, yellow needles, m. p. 107° (*acetyl* derivative, colourless needles, m. p. 88°), 5-chloro-3-amino-*o*-cresol, colourless needles, m. p. 107° (*hydrochloride*, leaflets; *diacetyl* derivative, needles, m. p. 196°), 4:5:6-trichloro-2:3-dihydroxytoluene, and 5-chloro-*o*-toluquinone 2-nitrate,



yellow crystals, m. p. 117—118°, by the methods described above. The last-mentioned compound is reduced by stannous chloride solution to 5-chloro-2:3-dihydroxytoluene, colourless needles, m. p. 89° (*diacetyl* derivative, needles, m. p. 65—66°), by stannous chloride

solution and concentrated hydrochloric acid to 5-chloro-6-amino-2:3-dihydroxytoluene, colourless leaflets, m. p. 150—160° (*hydrochloride*, needles; *triacetyl* derivative, needles, m. p. 183°; *tetraacetyl* derivative, leaflets, m. p. 135°), and by stannous chloride solution at 0° into 5-chloro-6-nitro-2:3-dihydroxytoluene, yellow needles and prisms, m. p. 135° (*diacetyl* derivative, colourless leaflets, m. p. 148°).

By chlorinating 5-chloro-6-amino-2:3-dihydroxytoluene hydrochloride in suspension in glacial acetic and concentrated hydrochloric acids a yellow keto-chloride is obtained, which by reduction in alcoholic solution with stannous chloride yields 5-chloro-2:3:6-trihydroxytoluene, colourless needles, m. p. 175°; this forms a *triacetyl* derivative, needles, m. p. 95°, and yields 5-chloro-2-hydroxy-p-toluquinone, pale red needles, m. p. 160°, by oxidation with nitric acid (D 1·15).

By treatment with nitric acid (D 1·48) at 0°, 4:5-dichloro-*o*-cresol yields 4:5-dichloro-3-nitro-*o*-cresol-nitroquinitrol,



colourless needles, m. p. 110° (decomp.), which yields 4:5-dichloro-*o*-toluquinone 2-nitrate (above) by boiling in tetrachloroethane solution and 4:5-dichloro-3-nitro-*o*-cresol by reduction with stannous chloride in methyl-alcoholic solution at 0°.

4-Chloro- and 6-chloro-*o*-cresols, by treatment with nitric acid, yield, not nitroquinitrols, but 4-chloro-3:5-dinitro-*o*-cresol, yellow needles, m. p. 146° (*acetyl* derivative, colourless needles, m. p. 109—110°), and 6-chloro-3:5-dinitro-*o*-cresol, yellow needles, m. p. 82—83° (*acetyl* derivative, colourless needles, m. p. 95°), respectively. C. S.

Chlorotrihydroxytoluenes. TH. ZINCKE and GRETE SCHÜRMANN (*Annalen*, 1918, **417**, 236—254).—3-Chloro-6-nitro-*o*-cresol, colourless needles, m. p. 79° (*acetyl* derivative, leaflets, m. p. 84°), prepared by treating 6-nitro-*o*-cresol in chloroform solution with the calculated quantity of chlorine, is converted by nitric acid (D 1·48) at 0° into 3-chloro-5:6-dinitro-*o*-cresol, stout, faintly yellow needles or prisms, m. p. 134° (*acetyl* derivative, colourless needles, m. p. 136°), which in alcoholic solution is reduced by stannous chloride solution to 3-chloro-5:6-diamino-*o*-cresol, colourless needles (*triacetyl* derivative, colourless needles, m. p. 236°), the *hydrochloride* of which, stout needles, by chlorination in glacial acetic and concentrated hydrochloric acids yields 1:3:3:4:4-pentachloro-2:5:6-triketo-1-methylcyclohexane, $\text{CMeCl} < \begin{matrix} \text{CO} \cdot \text{CCl}_2 \\ \text{CO} - \text{CO} \end{matrix} > \text{CCl}_2$, yellow plates, m. p. 68°. This keto-chloride is reduced by stannous chloride solution to 3-chloro-2:5:6-trihydroxytoluene, m. p. 175°, which is identical with the substance obtained by Zincke and Preiss from 3:5-dichloro-*o*-cresol-nitroquinitrol (preceding abstract).

By methods similar to the preceding, the following substances

have been prepared, starting with 4-nitro-*o*-cresol; 3-chloro-4-nitro-*o*-cresol, faintly yellow needles or leaflets, m. p. 74° (*acetyl* derivative, colourless needles or leaflets, m. p. 59°); 3-chloro-4:5-dinitro-*o*-cresol, faintly yellow needles, m. p. 139° (*acetyl* derivative, colourless needles, m. p. 167°); 3-chloro-4:5-diamino-*o*-cresol, colourless needles (*hydrochloride*, colourless needles, *triacetyl* derivative, needles, m. p. 230°, *azine* from phenanthraquinone, $C_{21}H_{18}ON_2Cl$, brownish-yellow leaflets, m. p. 273°); 1:3:3:6:6-pentachloro-2:4:5-triketo-1-methylcyclohexane, $C_7H_3O_3Cl_5$, pale yellow plates and prisms, m. p. 78°; and 3:6-dichloro-2:4:5-trihydroxytoluene, colourless needles, m. p. 155° (*triacetyl* derivative, needles, m. p. 151°). The last substance is oxidised by nitric acid (D 1.15), followed by acid, D 1.4, to 3:6-dichloro-4-hydroxy-*p*-toluquinone, red needles, m. p. 157°.

An alkaline solution of 3-chloro-4:5-diamino-*o*-cresol is oxidised by air to 3-chloro-4-amino-*p*-toluquinone-5-imide, $C_7H_7ON_2Cl$, red needles, m. p. 175—177° (decomp.; blackening at about 160°), which exhibits basic properties. 3-Chloro-4:5-diamino-*o*-cresol hydrochloride is oxidised by *N*-ferric chloride solution to 3-chloro-4-amino-*p*-toluquinone, dark red needles, m. p. about 142°, which is reduced by stannous chloride to 3-chloro-4-amino-2:5-dihydroxytoluene, colourless needles (*hydrochloride*, leaflets; *triacetyl* derivative, needles, m. p. 185°). C. S.

Organic Chemical Reagents. III. β -Phenylhydroxylamine and "Cupferron" (Ammonium Salt of Nitroso-phenylhydroxylamine). C. S. MARVEL and OLIVER KAMM (*J. Amer. Chem. Soc.*, 1919, **41**, 276—282. Compare A., 1918, i, 482; this vol., i, 61).—The statement made by various authors that β -phenylhydroxylamine is obtainable in theoretical yield by the reduction of nitrobenzene by means of zinc dust is inaccurate. Directions are now given for the reduction of nitrobenzene in portions of 500 grams, a yield of the dry product amounting to 64% of the theoretical being obtainable.

For the preparation of "cupferron," dry β -phenylhydroxylamine is not required, and the conditions are given under which the moist product is treated in ethereal solution with ammonia and amyl nitrite so as to obtain "cupferron" in a yield 80—90% of that theoretically possible. Even with the present high prices of materials and labour, "cupferron" may be made in the laboratory, where the labour charge is an abnormally high proportion of the total expenses, at a cost considerably less than the pre-war price of the product. [See *J. Soc. Chem. Ind.*, 1919, April.] T. H. P.

The Identification of Acids. IV. Phenacyl Esters. J. B. RATHER and E. EMMET REID (*J. Amer. Chem. Soc.*, 1919, **41**, 75—83).—In previous communications (A., 1917, i, 334, 559) the use of *p*-nitrobenzyl bromide for the identification of organic acids by the melting points of their *p*-nitrobenzyl esters was described. It is now shown that phenacyl bromide (ω -bromoacetophenone) may

be employed in a precisely similar manner and that in some cases the phenacyl esters of the acid are still more definitely characteristic than the *p*-nitrobenzyl esters. Phenacyl bromide is prepared by bromination of acetophenone in glacial acetic acid solution. The acid is neutralised with rather less than the theoretical quantity of sodium carbonate, and, working with 0.05 gram-mol. of the reagents, this quantity is dissolved in 5 c.c. of water, 1 gram of phenacyl bromide is added and then 10 c.c. of 95 per cent. alcohol. The ester is obtained after boiling for one hour with monobasic, two hours with dibasic, and three hours with tribasic acids. It is recrystallised from dilute alcohol until the melting point is constant. The following phenacyl esters have been characterised: acetate, m. p. 40°; aconitate, m. p. 90°; *o*-aminobenzoate, m. p. 181—182°; benzoate, m. p. 118.5°; *p*-bromobenzoate, m. p. 87°; cinnamate, m. p. 140.5°; citraconate, m. p. 108.5°; citrate, m. p. 104°; *m*-cresotate, m. p. 116.5°; *o*-cresotate, m. p. 138.5°; *p*-cresotate, m. p. 145.5°; fumarate, m. p. 197.5°; glutarate, m. p. 104.5°; itaconate, m. p. 79.5°; lactate, m. p. 96°; malate, m. p. 106°; maleate, m. p. 119°; *p*-nitrobenzoate, m. p. 128.4°; palmitate, m. p. 52.5°; pyrotartrate, m. p. 101.5°; saccharate, m. p. 120°; salicylate, m. p. 110°; stearate, m. p. 64°; succinate, m. p. 148°; tartrate, m. p. 130°.

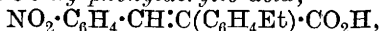
J. F. B.

Pschorr's Phenanthrene Synthesis. II. FRITZ MAYER and FRANK ALBERT ENGLISH (*Annalen*, 1918, **417**, 60—92. Compare Mayer and Balle, A., 1914, i, 536).—As the result of the experiments here recorded, it appears impossible to synthesise 8-, 5-, or 7-ethylphenanthrene by any of the methods at present known.

o-Ethylbenzyl alcohol, $C_6H_4Et \cdot CH_2 \cdot OH$, b. p. 229°, obtained by the electrolytic reduction of *o*-ethylbenzoic acid at a lead cathode in dilute sulphuric acid solution, is converted by cold saturated hydrobromic acid into *o*-ethylbenzyl bromide, colourless crystals, m. p. 34°, b. p. 225°/751 mm. The latter is converted by alcoholic sodium cyanide into *o*-ethylphenylacetonitrile, $C_6H_4Et \cdot CH_2 \cdot CN$, b. p. 257—258°/752 mm., which is hydrolysed by heating with 35% potassium hydroxide solution (2 mols.) and 30% hydrogen peroxide (3 mols.), yielding *o*-ethylphenylacetic acid, m. p. 83.5° (ethyl ester, a colourless, odourless oil). Attempts to reduce this acid to *o*-ethylbenzaldehyde, a colourless, odourless liquid, b. p. 210°/753 mm., by the methods of Mettler and Piria gave unsuccessful or unsatisfactory results, but the aldehyde is obtained in 67% yield by oxidising *o*-ethylbenzyl alcohol with potassium dichromate and 10% sulphuric acid, and in 33.6% yield by heating *o*-ethylbenzyl bromide with hexamethylenetetramine in 60% alcoholic solution. Further experiments were undertaken to ascertain the influence of negative substituents in the benzene nucleus on the Sommelet reaction. *o*-Nitrobenzyl chloride and hexamethylene-tetramine, boiled in 60% alcoholic solution for four hours, yielded, in addition to a small quantity of a substance, $C_{23}H_{15}O_7N_5$, m. p. 153.5°, a substance, m. p. 112°, which is regarded as *tri-o*-nitro-

benzyltrimethylenetriamine, $\text{NX} \begin{smallmatrix} \text{CH}_2 \cdot \text{NX} \\ \text{CH}_2 \cdot \text{NX} \end{smallmatrix} \text{CH}_2$ [where X is $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2$], since its molecular weight corresponds with this formula, and it yields formaldehyde and *o*-nitrobenzylamine hydrochloride by hydrolysis with boiling concentrated hydrochloric acid. In a similar manner, *p*-nitrobenzyl chloride and hexamethylenetetramine yield *tri-p-nitrobenzyltrimethylenetriamine*, m. p. 161°, whilst *o*- and *p*-chlorobenzyl chlorides yield *o*- and *p*-chlorobenzaldehydes respectively.

The attempt to condense *o*-ethylbenzaldehyde and sodium *o*-nitrophenylacetate by means of acetic anhydride and zinc chloride at 120° in an atmosphere of carbon dioxide yielded a very small quantity of a substance, $\text{C}_9\text{H}_9\text{O}_3\text{N}$, colourless crystals, m. p. 183·5°. A similar attempt to condense *o*-nitrobenzaldehyde and potassium *o*-ethylphenylacetate for two days at 100° yielded *β-o-nitrophenyl-α-o-ethylphenylacrylic acid*,



m. p. 194°. By reduction with ferrous sulphate and aqueous ammonia, it yields the corresponding *amino-acid*, colourless crystals, m. p. 178—179°, but the attempt to convert this into 8-ethylphenanthrenecarboxylic acid by shaking its diazotised solution with copper powder or by boiling with water yielded in the first case a non-crystallisable product, and in the second case *β-o-hydroxyphenyl-α-o-ethylphenylacrylic acid*, $\text{C}_{17}\text{H}_{16}\text{O}_3$, m. p. 205°.

The starting material in the attempt to synthesise 5- or 7-ethylphenanthrene is acetophenone, which by successive nitration and reduction yields *m*-aminoacetophenone. The latter is converted by hydrazine hydrate at 160° into a mixture of the *azine*, $\text{C}_{16}\text{H}_{18}\text{N}_4$, m. p. 147°, and the *hydrazone*, $\text{C}_8\text{H}_{11}\text{N}_3$, m. p. 98°, which is reduced by Wolff's sodium ethoxide method at 160° to *m*-ethylaniline; Staudinger and Kupfer's method of reduction with hydrazine hydrate at 210°, however, gives a greatly improved yield. *m*-Ethylaniline is converted by Sandmeyer's method into *m-ethylbenzonitrile*, $\text{C}_8\text{H}_7\text{Et} \cdot \text{CN}$, b. p. 116—117°/25 mm. This is hydrolysed to *m*-ethylbenzoic acid, from which, by methods similar to those used in the ortho-series above, are obtained in succession *m-ethylbenzyl alcohol*, b. p. 227°/758 mm., *m-ethylbenzyl bromide*, *m-ethylphenylacetoneitrile*, $\text{C}_8\text{H}_7\text{Et} \cdot \text{CH}_2 \cdot \text{CN}$, b. p. 250—254°/761 mm., *m-ethylphenylacetic acid*, m. p. 62—64°, and *m-ethylbenzaldehyde*, b. p. 212°.

Potassium *m*-ethylphenylacetate and *o*-nitrobenzaldehyde, condensed together by means of zinc chloride and acetic anhydride at 120° in an atmosphere of carbon dioxide, yield *β-o-nitrophenyl-α-m-ethylphenylacrylic acid*, m. p. 138°. This is reduced by ferrous sulphate and ammonia to the *amino-acid*, $\text{C}_{17}\text{H}_{17}\text{O}_2\text{N}$, m. p. 150—150·5°, the diazotised solution of which yields by boiling or by shaking with copper powder a mixture of *β-o-hydroxyphenyl-α-m-ethylphenylacrylic acid*, m. p. 203° (decomp.), and an *ethylphenanthrenecarboxylic acid*, $\text{C}_{17}\text{H}_{14}\text{O}_2$, m. p. 147—149°, which is

probably 5-ethylphenanthrene-9-carboxylic acid. Attempts to convert the latter into ethylphenanthrene by heating under ordinary or reduced pressure were unsuccessful. C. S.

Hydroxy-carbonyl Compounds. I. New Synthesis of Hydroxy-aldehydes. P. KÄRRER (*Helv. Chim. Acta*, 1919, **2**, 89—94).—A rapid current of hydrogen chloride is passed for several hours into dry ether containing resorcinol, cyanogen bromide, and anhydrous zinc chloride. The crystals of the intermediate product, which contains chlorine, but not bromine, are collected and dissolved in cold water, and the solution, after being washed with ether, is boiled for twenty minutes. The 2:4-dihydroxybenzaldehyde, which is thus produced in good yield, is extracted with ether. It appears to be formed by the reactions: (i) $\text{CBrN} + \text{HCl} = \text{CHBr:NCl}$; (ii) $\text{CHBr:NCl} + \text{C}_6\text{H}_4(\text{OH})_2 = \text{C}_6\text{H}_3(\text{OH})_2\text{:CH:NCl} + \text{HBr}$; (iii) $\text{C}_6\text{H}_3(\text{OH})_2\text{:CH:NCl} \xrightarrow{\text{H}_2\text{O}} \text{C}_6\text{H}_3(\text{OH})_2\text{:CHO}$.

Phloroglucinol reacts in a similar manner.

C. S.

Phenols Insoluble in Alkali Hydroxides. ROGER ADAMS (*J. Amer. Chem. Soc.*, 1919, **41**, 247—270).—Investigation has been made of the phenylhydrazones of the *o*-hydroxyaldehydes and ketones in order to determine the structure characteristic of such compounds of this type as are insoluble in alkali hydroxides. The results show that the introduction of a methyl group, or, in general, of a group containing carbon, into either the phenolic ring or the side-chain of one of these phenylhydrazones is accompanied by marked depression of the solubility of the compound in 10% aqueous sodium hydroxide. A bromine atom produces a less effect, which is the more noticeable with substitution in the side-chain. When a nitro-group is introduced into the phenolic ring in the ortho- or para-position to the hydroxyl group, the solubility in alkali is increased, and a nitro-group in the para-position in the phenylhydrazone residue has the same effect. This result is regarded as due to the possibility of the rearrangement of nitrophenols and of *p*-nitrophenylhydrazones to aci-nitro-compounds, which are readily soluble in alkali. Where there is no tendency to form aci-nitro-compounds, as with the *m*- and *o*-nitrophenylhydrazones, the nitro-group has the same effect as other groups and increases the insolubility in alkali hydroxides. No compound with a nitro-group in the meta-position to the hydroxyl was prepared, but such a compound should show diminished solubility in alkali. Comparison of the phenylhydrazones of *p*-homosalicylaldehyde and pæonol with the corresponding hydrazones, the former being insoluble and the latter soluble in alkali hydroxides, shows that a large group like phenyl in the hydrazone residue is absolutely necessary for the compound to show insolubility in alkali. The marked effect of a methyl or phenyl group attached to the carbon atom carrying the phenylhydrazone residue, as compared with a hydrogen atom, is shown by the perfect solubility of the azines of *p*-homosalicyl-

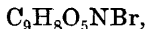
aldehyde and β -naphthaldehyde in cold alkali hydroxide solution and the insolubility of the azines of pæonol and 2-hydroxy-5-methylbenzophenone in boiling alkali. Finally, a substituent group attached to the iminic nitrogen has a decided effect in reducing the solubility in alkali hydroxides.

The various explanations which have been advanced to account for the insolubility of these phenolic compounds in alkali hydroxide solution are discussed and shown to be unsatisfactory, and the author regards this behaviour as due to the fact that such compounds are very weak acids and highly insoluble in water. Any insoluble, slightly hydrolysed acid would be expected to behave similarly, and the introduction into its molecule of a positive or negative atom or group will have a result determined by two distinct effects: first, the insolubility in water due to the increased size of the whole molecule, this leading to increased insolubility in alkali hydroxide, and, secondly, an increase or a decrease in the acidity of the whole molecule, depending on the nature and position of the group introduced.

Pæonol phenylhydrazone is soluble in hot alkali solution; the *hydrazone*, $C_9H_{12}O_2N_2$, white plates, quickly turning yellow on exposure, m. p. $73-75^\circ$, dissolves in cold alkali hydroxide; the *azine*, $C_{18}H_{20}O_4N_2$, lemon-yellow crystals, m. p. $226-227^\circ$, is insoluble in boiling alkali hydroxide; the 2:4:6-*tribromophenylhydrazone*, $C_{15}H_{12}O_2N_2Br_3$, white needles, m. p. 162° , is insoluble in boiling alkali hydroxide.

Bromopæonol, $C_9H_9O_3Br$, has m. p. 169° (Brüll and Friedländer, A., 1897, i, 221, gave 171°); its *phenylhydrazone*, $C_{15}H_{15}O_2N_2Br$, slender, yellow needles, m. p. $172.5-173.5^\circ$, its *p-bromophenylhydrazone*, dull yellow, monoclinic plates, m. p. 189.5° , and its 2:4:6-*tribromophenylhydrazone*, white needles, m. p. $169-171^\circ$, are insoluble in boiling alkali hydroxide. Its *methyl ether*, $C_{10}H_{11}O_3Br$, forms white needles, m. p. $139-140^\circ$; neither this methyl ether nor that of pæonol itself yields a phenylhydrazone in the ordinary way.

ω -*Tribromobromopæonol*, $OH \cdot C_6H_2Br(OMe) \cdot CO \cdot CBr_3$, forms lemon-yellow needles, m. p. $123-124^\circ$. *Bromonitropæonol*,

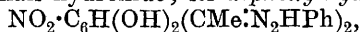


forms long, hairy needles, m. p. $112-114^\circ$; its *phenylhydrazone*, $C_{15}H_{14}O_4N_3Br$, forms saffron-coloured crystals, m. p. $204.5-205.5^\circ$, and dissolves gradually in cold, readily in warm alkali. *Nitropæonol*, $C_9H_9O_5N$, forms white needles, m. p. 155° ; its *phenylhydrazone*, $C_{15}H_{15}O_4N_3$, orange needles, m. p. $215.5-216.5^\circ$, is soluble slightly in cold, readily in warm alkali hydroxide; its *methyl ether*, $C_{10}H_{11}O_5N$, forms slender, white needles, m. p. 131° , gradually turning yellowish-red. *Aminopæonol*, $C_9H_{11}O_5N$, forms greenish-yellow, monoclinic prisms, m. p. $112-113^\circ$; its *platinichloride* was prepared and analysed.

Dinitroacetylresacetophenone, $C_6HAc(OH)(OAc)(NO_2)_2$, forms white plates, m. p. $121-122^\circ$. *Dinitroresacetophenone*,



forms pale yellow crystals resembling fine sand, m. p. 166—167°, and its *phenylhydrazone*, $C_{14}H_{12}O_6N_4$, reddish-brown crystals, darkening at 238° and decomposing at 242.5°. *Acetylaminoresacetophenone*, $C_8H_2Ac(OH)_2 \cdot NHAc$, forms white needles, m. p. 254°. *Nitroresodiacetophenone*, $C_8HAc_2(OH)_2 \cdot NO_2$, forms white needles, m. p. 231°; its *phenylhydrazone*, $C_{16}H_{15}O_5N_3$, pale yellow powder, darkening at 220° and decomposing sharply at 235°, is soluble in cold alkali hydroxide; its *diphenylhydrazone*,

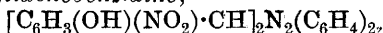


massive, lemon-yellow needles, becoming orange-red and decomposing at 273°, dissolves slightly in cold and readily in warm alkali hydroxide.

Bromoresodiacetophenone, $C_{10}H_9O_4Br$, forms white plates, m. p. 205°.

Salicylaldehyde *o*-tolylhydrazone dissolves in alkali hydroxide only in the hot; the 2:4:6-tribromophenylhydrazone, white needles, m. p. 100°, dissolves gradually, with decomposition, in boiling alkali hydroxide.

Di-5-nitrosalicylidenebenzidine,



forms red crystals not melting below 275° and dissolves partly in boiling alkali hydroxide. *Di-3-nitrosalicylidenebenzidine* forms bright red crystals not melting below 275°, and is somewhat more soluble in boiling alkali hydroxide than the 5-isomeride.

p-Homosalicylaldehydephenylhydrazone is soluble in hot alkali hydroxide; the *hydrazone*, $C_8H_{10}ON_2$, white powder, m. p. 72—74°, dissolves in cold alkali hydroxide.

Bromo-p-homosalicylaldehyde, $C_8H_7O_2Br$, forms yellow crystals shrinking at 63°, m. p. 65°, and its *phenylhydrazone*, $C_{14}H_{13}ON_2Br$, dirty yellow crystals, m. p. 140—141°, soluble in hot alkali hydroxide.

5-*Methyl-2-hydroxybenzophenoneazine*, $[C_6H_3Me(OH) \cdot CPh]_2N_2$, forms lemon-yellow crystals, m. p. 259—260°, and is insoluble in boiling sodium hydroxide solution.

T. H. P.

Pinacolin Transformations. IV. Ring Changes produced by the Elimination of Water from Alicyclic Alcohols.

HANS MEERWEIN (*Annalen*, 1918, 417, 255—277. Compare A., 1914, i, 850).—In connexion with the previous investigation (*loc. cit.*), 1-methyl-1- α -hydroxyethylcyclopentane has been synthesised and also submitted to the dehydrating action of zinc chloride, and the constitution of the resulting hydrocarbon has been determined; it is 1:2-dimethyl- Δ^1 -cyclohexene, and the reaction is one of the smoothest changes known of a cyclopentane into a cyclohexane derivative.

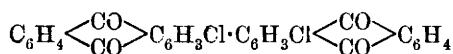
[With CL. FLEISCHHAUER.]—The reaction between magnesium and 1-chloro-1-methylcyclopentane in ether at 5—10°, preferably in the absence of air, and treatment of the product with carbon dioxide and subsequently with ice-water and dilute sulphuric acid, lead to the formation of 1-methylcyclopentane-1-carboxylic acid,

the acid chloride of which reacts with magnesium methyl iodide in ether at -15° to form, after the usual treatment, 1-methyl-1-cyclopentyl methyl ketone, $C_5H_8Me \cdot COMe$, b. p. $48.4^{\circ}/10$ mm., in good yield, the semicarbazone of which forms colourless needles, m. p. $143-144^{\circ}$. By reduction with sodium and moist ether, the ketone yields 1-methyl-1- α -hydroxyethylcyclopentane, $C_5H_8Me \cdot CHMe \cdot OH$, b. p. $67.6^{\circ}/10.5$ mm., together with the corresponding pinacone, $C_{16}H_{30}O_2$, colourless prisms, m. p. $89-90^{\circ}$, the former of which yields only 1:2-dimethyl- Δ^1 -cyclohexene by heating with zinc chloride at $180-190^{\circ}$.

The acid chloride of 1:2:2:3-tetramethylcyclopentane-1-carboxylic acid reacts with zinc methyl or, better, magnesium methyl iodide in ether to form, ultimately, 1:2:2:3-tetramethyl-1-cyclopentyl methyl ketone, $C_{11}H_{20}O$, b. p. $101-102^{\circ}/18$ mm. (semicarbazone, m. p. 232°), which is reduced by sodium and moist ether to 1:2:2:3-tetramethyl-1- α -hydroxyethylcyclopentane, $C_{11}H_{22}O$, b. p. $108-109^{\circ}/15$ mm. The alcohol appears to be a mixture of two stereoisomeric forms, since it partly solidifies, the solid form having m. p. $70-71^{\circ}$, D_4^{20} 0.9113 (supercooled), n_D^{20} 1.46322. By heating with zinc chloride, the alcohol yields a mixture of 1:2:3:3:4-pentamethyl- Δ^1 -cyclohexene (chief product) and 1:2:2-trimethyl-3-isopropyl- Δ^2 -cyclopentene, the constitutions of which are deduced from the nature of the products of the decomposition of the ozonides. C. S.

mesoNaphthodianthrone. ALFRED ECKERT and RUDOLF TOMASCHEK (*Monatsh.*, 1918, **39**, 839-864).—The authors have endeavoured to synthesise derivatives of mesonaphthodianthrone in a manner which leaves no doubt as to their constitution. For this purpose the method of Scholl, Mansfield, and Potschiwuscheg (*A.*, 1910, i, 494) as modified by Ullmann and Minajeff (*A.*, 1912, i, 366) has been applied to certain *aa'*-dichloroanthraquinones; of these only the 1:4-derivative reacts with copper powder, the 1:5- and 1:8-dichloro- and the 1:4:5:8-tetrachloro-products remaining unattacked. The procedure of Meyer, Bondy, and Eckert (*A.*, 1913, i, 62) is not applicable to halogenated anthraquinones, since the halogen is partly eliminated during reduction with zinc and alkali. A more successful process consists in converting the anthranols into the corresponding dihydrodianthrone, enolisation of the latter (enolisation by alkali occurs less readily with derivatives than with the parent substance and the products are considerably less stable), and oxidation of the material so formed to the dianthrone; the latter is converted into the corresponding mesonaphthodianthrone when exposed to light. In cases in which formation of the mesonaphthalene ring cannot occur by simple elimination of hydrogen, a peculiar phenomenon is observed; when dissolved in nitrobenzene or xylene, the substance is unchanged after protracted illumination, whilst in concentrated sulphuric acid solution elimination of two atoms of hydrogen and two of chlorine slowly occurs.

4:4'-Dichloro-1:1'-dianthraquinonyl,



pale yellow crystals, is reduced by copper powder and concentrated sulphuric acid to 4:4'-dichloromesobenzdianthrone, yellowish-brown needles, which under the action of light pass into 4:4'-dichloromesonaphthdianthrone, $\text{CO} \begin{array}{c} \diagup \text{C}_6\text{H}_2\text{Cl} \\ \diagdown \text{C}_6\text{H}_3 \end{array} \text{C} = \text{C} \begin{array}{c} \diagup \text{C}_6\text{H}_2\text{Cl} \\ \diagdown \text{C}_6\text{H}_3 \end{array} \text{CO}$, small, yellow needles.

1(or 4)-Chloroanthrone, yellow needles, m. p. 106°, obtained by the reduction of 1-chloroanthraquinone by aluminium bronze and sulphuric acid, is oxidised by ferric chloride to 4:4'-dichlorodihydrodianthrone, colourless crystals which darken without melting at 270°. The enolic form of this substance is an unstable, green powder, which is readily converted by persulphate into 4:4'-dichlorodianthrone, greenish-yellow crystals, from which 4:4'-dichloromesonaphthdianthrone is obtained by exposure to light.

1:4-Dichloroanthrone, yellow needles, m. p. 136—138°, 1:4:1':4'-tetrachlorodihydrodianthrone, colourless crystals, m. p. 250° (decomp.), and 1:4:1':4'-tetrachlorodianthrone, yellow plates, are prepared by a similar series of reactions; the latter substance loses two atoms of hydrogen and two of chlorine when its solution in concentrated sulphuric acid is exposed to light, but the product obtained did not give sharp analytical results.

1:5-Dichloroanthrone yields 1:5:1':5'-tetrachlorodihydrodianthrone, colourless crystals, and 1:5:1':5'(or 4:8')-tetrachlorodianthrone, yellow platelets; the corresponding mesonaphthdianthrone could not be obtained in the pure state. Similarly, 1:8-dichloroanthrone, yellow needles, m. p. 115°, 4:5:4':5'-tetrachlorodihydrodianthrone, colourless crystals which remain unchanged up to 280°, 4:5:4':5'-tetrachlorodianthrone, pale yellow crystals, and 4:5:4':5'-tetrachloromesonaphthdianthrone, small, yellow needles, were prepared.

3:3'-Dibromomesobenzdianthrone forms a reddish-yellow, crystalline powder which is converted by light into 3:3'-dibromomesonaphthdianthrone, pale yellow powder.

Starting from 1:3-dichloroanthraquinone (Meyer and Zahn, A., 1913, i, 455), the constitution of which is now definitely established by its conversion into 1:3-diphenoxyanthraquinone (Ullmann and Eiser, A., 1916, i, 823), the following series of substances is obtained: 3:3'-dichloro-1:1'-dianthraquinonyl, greenish-yellow needles, 3:3'-dichloromesobenzdianthrone, yellowish-brown needles, and 3:3'-dichloromesonaphthdianthrone, small, yellow needles. Attempts to prepare the substance last named from 2-chloroanthraquinone led to a different product through the following stages: 2-chloroanthrone, yellow needles, m. p. 115—120°, which are readily oxidised; 3:3'(3:2')-dichlorodihydrodianthrone, silvery, crystalline powder, m. p. 240° (decomp.); 3:3'(3:2')-dichlorodianthranol, greenish-yellow, crystalline powder; dichlorodianthrone, yellow,

crystalline powder, in which the position of the chlorine atoms is not decided; and (3:6')-dichloromesonaphthadanthrone, small, yellow needles. H. W.

Constitutions of the Fenchene Hydrocarbons. WALTER QVIST (*Annalen*, 1918, **417**, 278—324).—The author has examined the fenchenes obtained by different methods and having b. p.'s below 150°. He shows that Aschan was right in stating that β -pinolene (*cyclofenchene*) occurs in the fenchene fraction, b. p. below 150°, obtained from fenchyl chloride. Kondakov and Lutschinin's hydrocarbon (A., 1907, i, 713) is not β -pinolene, but is identical with the author's *isofenchylene*.

When *DL*-fenchyl alcohol is heated with aluminium phosphate at 210° or with potassium hydrogen sulphate at 200°, the hydrocarbons obtained contained *d*- β -fenchene and a little *l*- α -fenchene in the fraction of high b. p. (152—155°) and *d*-*cyclofenchene* and *i*-isofenchylene in the fractions, b. p. 141—143° and 143—145°. *d*-*cyclo*Fenchene is also obtained by heating *DL*-fenchyl xanthate at 230°, *l*- α -fenchene also being produced. Since both these hydrocarbons yield the same hydrochloride, which yields *l*- α -fenchene by heating with *o*-toluidine, the xanthate method is an excellent means of preparing pure *l*- α -fenchene.

Very pure *d*- β -fenchene (*dibromide*, $C_{10}H_{16}Br_2$, crystals, m. p. 81—82°, $[\alpha]_D^{25} -31.2^\circ$ in ethyl acetate) is obtained by heating *l*-isofenchyl chloride with *o*-toluidine. By the xanthate method *l*-isofenchyl alcohol yields *l*-isofenchylene.

β -Pinolene yields two dibromides, namely, *l*- and *i*- α -fenchene dibromides. This proves that Aschan's β -pinolene and the author's tricyclic hydrocarbon obtained from *DL*-fenchyl alcohol are identical, with the difference, however, that the latter is feebly dextro-rotatory *d*-*cyclofenchene* whilst the former is a mixture of *l*-*cyclo*-fenchene and *dl*-*cyclofenchene*.

The reduction of *d*- α -fenchene dibromide by zinc dust and 75% alcohol at 55° yields fenchane and *l*- α -fenchene. As these two hydrocarbons contain different skeletons, no conclusions can be drawn as to the constitution of the α -fenchene dibromide. C. S.

Phenylurethanes of Terpene Alcohols and Phenols. F. WEEHUIZEN (*Pharm. Weekblad*, 1919, **56**, 299—301).—The terpene alcohol or phenol is dissolved in petroleum (distilling between 170° and 200°). The requisite quantity of phenylcarbimide is added and the solution boiled. On cooling, the phenylurethane crystallises out in quantitative yield and is recrystallised from benzene (80—100°). The phenylurethanes of the following substances were prepared: *o*-, *m*-, *p*-cresol (m. p. 141°, 121—122°, 111—112° respectively), thymol (m. p. 106—107°), menthol (m. p. 111—112°), borneol (m. p. 137—138°), eugenol (m. p. 95°).

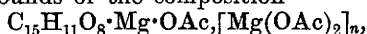
The method may be used for the separation of camphor and borneol. The former is unacted on and remains in solution; the latter separates out as bornylphenylurethane. W. S. M.

Constituents of Resins. IV. β -Dammar-resin. ALOIS ZINKE and ERNA UNTERKREUTER (*Monatsh.*, 1918, **39**, 865—869).—Analyses and determinations of molecular weight show the hydrocarbon portion of β -dammar-resin (compare Dulk, *Jahrb. pr. Chem.*, 1848, **45**, 16; Tschirch and Glimmann, A., 1896, i, 164) to have the composition $C_{30}H_{48}$; it melts indefinitely at 195° after softening from 165° , and possibly represents a mixture of hydrocarbons. Attempts have been made to prepare derivatives of it by oxidation, action of nitrous acid, and action of ethereal hydrogen chloride, but definite products have not been isolated. H. W.

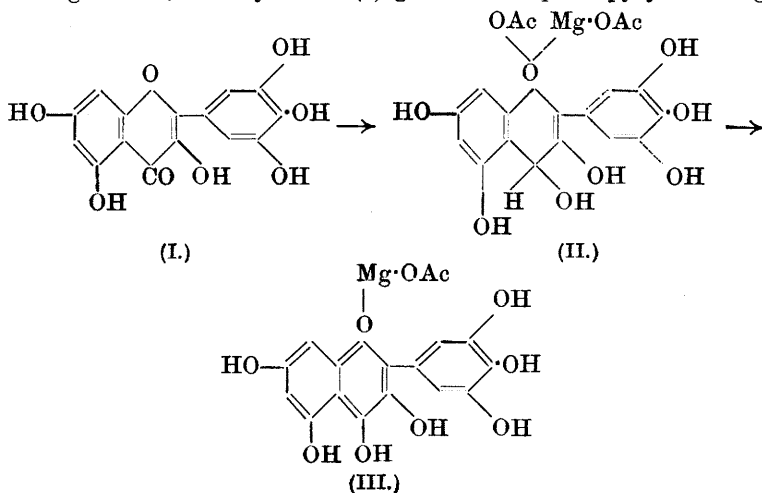
Biochemical Synthesis, by means of Emulsin, of α -Naphthylcarbiny- β -glucoside. EM. BOURQUELOT and M. BRIDEL (*Compt. rend.*, 1919, **168**, 323—324).—When emulsin acts on an acetone solution of dextrose and α -naphthylcarbinol, α -naphthylcarbiny- β -glucoside, long needles, m. p. 156 — 157° (corr.), $[\alpha]_D -71.02^\circ$, is obtained, which is readily hydrolysed by emulsin or by dilute sulphuric acid. W. G.

Anthocyanins : Colour Variation in Anthocyanins. KEITA SHIBATA, YUJI SHIBATA, and ITIZO KASIWAGI (*J. Amer. Chem. Soc.*, 1919, **41**, 208—220).—For the reduction of compounds of the flavone and flavanol series, organic acids may be used in conjunction with zinc or magnesium in place of inorganic acids. With monobasic acids deep green to bluish-green pigments are mostly obtained, the tints varying slightly according to the reagents employed. Some of these pigments were isolated and their properties examined.

When reduced with magnesium and glacial acetic acid, myricetin gives green compounds of the composition

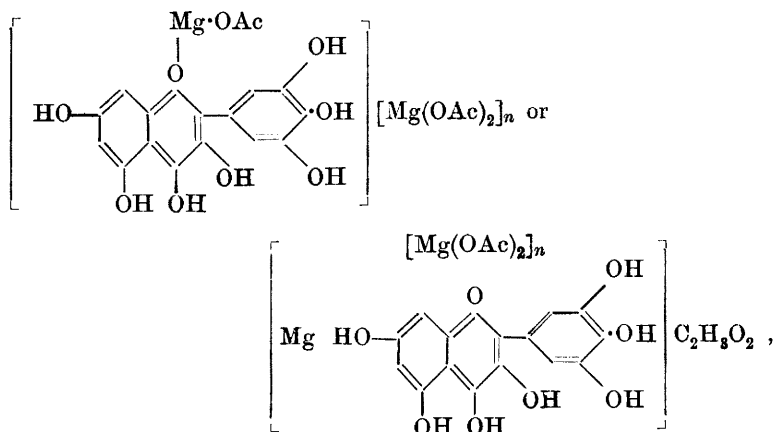


n being 2 or 4; the myricetin (I) gives first a phenopyrylium ring



(II), the organo-metallic compound (III) then resulting by elimination of acetic acid from the ring.

As the acetates of the bivalent metals often tend to form complex compounds, it was to be expected that addition of magnesium acetate would take place, giving:



according to Werner's co-ordination theory.

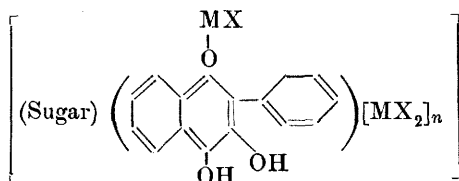
Similarly, myricitrin, a rhamnoside of myricetin, gives with the same reagents a deep blue product co-ordinated with four molecules of magnesium acetate.

The above green or blue pigments are soluble in water as well as in alcohol, giving neutral solutions with the same colours, but the addition of dilute acid (hydrochloric) to the solutions changes the colour to red, the $\cdot\text{Mg} \cdot \text{OAc}$ group of the green pigment (III) being replaced by a chlorine atom in the red oxonium salt. This explains why Willstätter and others have always obtained red pigments by reduction of the yellow pigments. Even with inorganic acids green or blue pigments are formed under certain conditions, treatment of myricetin with alcoholic hydrochloric acid yielding a deep green pigment in the molecule of which the position of the $\text{Mg} \cdot \text{OAc}$ group (III) is occupied by $\cdot\text{MgCl}$; here addition of magnesium chloride does not take place, probably because of its smaller tendency to form complex salts. The compound dissolves in water and alcohol, giving neutral solutions of the original colour.

That all the above compounds have deep colours or, in other words, that their absorption bands are displaced far towards the red end of the spectrum, is attributed on the one hand to the fact that the phenylpyrylium ring of the green or blue pigments has one more hydroxyl group than that of the oxonium salts, and on the other to the fact that magnesium forms the complexes with its auxiliary valence, which together play the rôle of bathochromism. In the case of the reduced glucoside, flavanol, one of the hydroxyl groups is replaced by a sugar molecule, which shifts the absorption

band hypsochromatically, that is, towards the violet end of the spectrum.

From these results and those of experiments on the pigments of many flowers, the following explanation of the various flower colours is based. The metal organic or complex compounds of reduced flavanol glucosides (annexed formula) are the most important factor in the production of flower colours. The "blue" anthocyanins are the complex compounds of reduced flavanol glucosides, which possess several hydroxyl groups belonging to the flavanol nucleus besides those of sugar molecules, and the metal with which they are



co-ordinated is probably calcium or magnesium, as salts of these metals are always present in the plant cells. The "violet," "violet red," or "red" pigments are either the analogous metallic complex compounds of flavanol glucosides, which contain fewer of the auxochrome hydroxyl groups, or a mixture of the blue pigments and their products of decomposition by excess of acids, that is, Willstätter's red oxonium salts.

This theory is confirmed by the behaviour of the natural anthocyanin solutions towards the salts of alkaline earth and heavy metals, addition of the latter to alcoholic extracts of various flowers always acting bathochromatically.

Experimental details are given.

T. H. P.

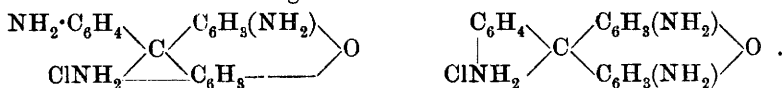
A New Yellow Dye and Light Filters made from It.

C. E. K. MEES and H. T. CLARKE (*Brit. J. Photo.*, 1919, **66**, 48).—The new dye is the *glucosazone* formed by the condensation of dextrose with *p*-hydrazinobenzoic acid; it gives a very soluble sodium salt.

W. G.

Composition of Pyrocresoles and their Relationship to Coal Tar Constituents. FRIEDRICH RUSZIG (*Zeitsch. angew. Chem.*, 1919, **32**, [i], 37–40).—The so-called isomeric pyrocresoles, isolated by Schwarz (A., 1883, 204; 1884, 79) from the residue of the distillation of crude phenol, have the same composition, $\text{C}_{15}\text{H}_{14}\text{O}$, and properties as the compounds prepared by Gladstone and Tribe (T., 1889, **55**, 51) by the decomposition of the aluminium *o*-, *m*-, and *p*-tolyl oxides. They have been identified as dimethylxanthen, whilst the homologous compound, $\text{C}_{13}\text{H}_{10}\text{O}$, is xanthen, produced by the decomposition of aluminium phenoxide in accordance with the equation $2\text{Al}(\text{O}\cdot\text{C}_6\text{H}_5)_3 = (\text{C}_6\text{H}_5)_2\text{O} + \text{C}_{13}\text{H}_{10}\text{O} + \text{C}_6\text{H}_5\cdot\text{OH} + \text{CH}_4 + \text{C}_4 + \text{Al}_2\text{O}_3$. From aluminium *m*-tolyl oxide, two isomeric dimethylxanthen, corresponding with Schwarz's α - and β -pyrocresoles, were prepared, but the third isomeric modification was not found.

Aluminium *p*-tolylxide yielded symmetrical *p*-dimethylxanthen (m. p. 168°), whilst from aluminium *o*-tolylxide the 4:5-dimethylxanthen was obtained. The liquids of high boiling point which separate at the end of the distillation of aluminium phenoxide have the composition $C_{19}H_{14}O$, and appear to be formed from xanthen, as follows: $C_{13}H_{10}O + C_6H_5 \cdot OH = C_{19}H_{14}O + H_2O$. On dissolving this compound in nitric acid and adding water, an amorphous, yellow compound is precipitated. By reducing this with zinc and acetic acid, and precipitating the base with ammonia, a brown colouring matter is obtained. Its hydrochloride is soluble in water and acts as a direct brown dye for wool and silk. This dye, for which the name xanthen-brown is suggested, is an inner ester of magenta and has a constitution corresponding with one of the following formulæ:



Analogous compounds obtained in the distillation of aluminium tolyloxides had the composition of tolyldimethylxanthenes and also yielded xanthen-browns, and similar compounds were obtained from the anthracene oils of coal tar, which probably consist, in part, of triphenylmethane derivatives, and, in particular, of phenyl- and diphenyl-xanthenes. [See also *J. Soc. Chem. Ind.*, 1919, April.]

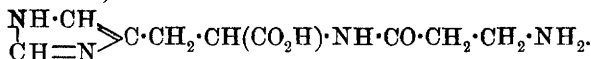
C. A. M.

Synthesis of Aminoflavones, of Flavone-azo- β -naphthol Dyes and of other Flavone Derivatives. MARSTON TAYLOR BOGERT and JOSEPH K. MARCUS (*J. Amer. Chem. Soc.*, 1919, **41**, 83—107).—Flavone was prepared by a modification of Ruhemann's method (A., 1913, i, 891), using smaller quantities of aluminium chloride and benzene. Nitration in the cold by nitric and sulphuric acids in glacial acetic acid solution yielded mixtures which were separated into two fractions, consisting of 2'- and 3'-nitroflavones and of 3'- and 4'-nitroflavones. These were converted by reduction with stannous chloride into the aminoflavones, the three isomerides being separated and purified by taking advantage of their different basicities and solubilities. 2'-Aminoflavone crystallises from hot acetone in silky, pale yellow needles, m. p. 149·5—150·5° (corr.); 3'-aminoflavone crystallises from pyridine or xylene in lemon-yellow, straight needles, m. p. 156—157° (corr.), and 4'-aminoflavone crystallises from the same solvents in long, golden-yellow needles, m. p. 234—236° (corr.). From the three aminoflavones, the corresponding hydroxyflavones were prepared by means of the diazonium salts, and were decomposed by sodium ethoxide and alcohol into *o*-hydroxyacetophenone and *o*-, *m*-, and *p*-hydroxybenzoic acids, owing to the rupture of the pyrone ring at the double bond. 2'-Hydroxyflavone forms lustrous, colourless plates, m. p. 249—250° (corr.). The three aminoflavones have been diazotised and coupled with β -naphthol to form flavoneazo- β -naphthols, m. p. 265—266·5°, 257°, and 274—275° (corr.) respectively, giving

orange to red shades on silk and wool, extremely fast to light and alkalis. Other compounds obtained are 2'-*acetoxyflavone*, m. p. 88·5—89° (corr.), 2'-*diacetylaminoflavone*, m. p. 186·5—187·5° (corr.), 3'-*diacetylaminoflavone*, m. p. 231—232° (corr.), 4'-*diacetylaminoflavone*, m. p. 246—248° (corr.), β -*phenoxy- β -phenylpropionic acid*, m. p. 150—151° (corr.), the barium salt of a disulphonic derivative of the latter acid, and *methyl β -bromo- β -phenylpropionate*, m. p. 37·5—38·5° (corr.). It is noted that whereas all the hydroxyflavones are colourless, all the aminoflavones are yellow, thus indicating the more powerful auxochromic effect of the amino-group in this series; also 4'-aminoflavone possesses the remarkable property of fluorescence only in neutral solvents which contain the hydroxyl group.

J. F. B.

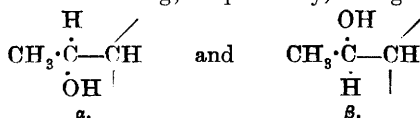
Carnosine, Constitution and Synthesis. GEORGE BARGER and FRANK TUTIN (*Biochem. J.*, 1918, 12, 402—407).—2:4:5-Trinitrotoluene condenses with amino-acids when boiled in dilute alcoholic solution, the amino-acid becoming attached to the benzene ring by its amino-group, which replaces the reactive nitro-group in position 5. This reaction does not occur with imino-groups, but does take place with the free amino-groups of peptides. The condensation product of 2:4:5-trinitrotoluene with carnosine on hydrolysis yields dinitrotolyl- β -alanine, thus proving carnosine to be β -alanylhistidine,



For the synthesis of carnosine, β -nitropropionyl chloride, b. p. 123°/10 mm., was condensed with histidine methyl ester, and the resulting very unstable product was at once reduced by stannous chloride and dilute hydrochloric acid, and the carnosine isolated as its copper salt.

W. G.

The α - and β -Hydroxydihydrocinchonines and their Rôle in the Production of certain Isomerides of Cinchonine. E. LÉGER (*Compt. rend.*, 1919, 168, 404—407).—The so-called β -hydroxycinchonine, like its α -isomeride (compare A., 1918, i, 304), when acted on by 50% sulphuric acid gives a mixture of cinchonigine, cinchoniline, and apocinchonine. The ratio of cinchonigine to cinchoniline obtained from the β -isomeride is practically the inverse of that obtained from the α -isomeride, but if the strength of the acid is increased to 70% and the heating prolonged to twenty-four hours, the proportions of these two bases are almost the same from each isomeride. From this, the author concludes that β -hydroxycinchonine, like the α -isomeride (*loc. cit.*), is a product of the addition of the elements of water to cinchonine, the two isomerides containing, respectively, the groupings



W. G.

Nicotinic Acid Derivatives. II. Guvacine and *iso*Guvacine.

E. WINTERSTEIN and A. B. WEINHAGEN (*Zeitsch. physiol. Chem.*, 1918, **104**, 48—53. Compare A., 1918, i, 35).—In view of recent publications on the same subject (Hess and Liebbrandt, A., 1918, i, 401; Hess, *ibid.*, 403; Freudenberg, *ibid.*, 403), the authors submit a short account of their experiments, fuller details being promised in a later paper. They are led to the conclusion that guvacine is in all probability Δ^3 -tetrahydronicotinic acid (contrast Trier, A., 1913, i, 803), whereas *isoguvacine* is a simple derivative of pyrrole.

The following details are given. Guvacine crystallises in prisms, m. p. 293—295°, is neutral to litmus, and optically inactive. The hydrochloride, platinichloride, and aurichloride have m. p.'s 312°, 233°, and 195—197° respectively; nitrosoguvacine forms needles, m. p. 167°. Reduction of guvacine with hydrogen in the presence of platinum leads to the formation of dihydroguvacine, m. p. 252° (hydrochloride, m. p. 237°; platinichloride, m. p. 233—235°; aurichloride, prismatic needles, m. p. 193—195°; mercurichloride, m. p. 230—231°), which is shown to be identical with hexahydronicotinic acid. Methylation of guvacine leads to the formation of *N*-dimethylguvacine, m. p. 225° (?) [hydrochloride, m. p. 256—258°; platinichloride, m. p. 253°; aurichloride, m. p. 224—226°; picrate, m. p. 224—225°; mercurichloride, m. p. 174—176°], which is found to be identical in all respects with the arecadinemethylbetaine described by Willstätter (A., 1897, i, 385).

*iso*Guvacine has m. p. 220°, is faintly acid to litmus, and is optically inactive. The hydrochloride, m. p. 231° (decomp.), platinichloride, m. p. 235° (decomp.), and aurichloride, m. p. 198—200°, are described. When the base is heated with zinc dust, an intense odour of pyrrole is observed, and a pine shaving dipped in concentrated hydrochloric acid is coloured intensely red. *iso*Guvacine is slowly reduced by hydrogen in the presence of platinum, but the hydrochloride of the new base is not uniform: the platinichloride has m. p. 225°. *iso*Guvacine forms a dimethyl derivative, the platinichloride of which has m. p. 252°. H. W.

Ring Formation with Elimination of a Nitro-group.

S. REICH and (MLLE.) V. NICOLAËVA (*Helv. Chim. Acta*, 1919, **2**, 84—88).—The reaction examined by Reich with Gaigallian (A., 1917, i, 595) and with Turkus (*ibid.*, i, 585) has been further studied. Whilst the phenylhydrazones of ethyl 2:4-dinitrophenylglyoxylate, of 2:6-dinitrobenzaldehyde, and of 2-chloro- or 2-bromo-6-nitrobenzaldehyde yield *iso*indazole derivatives with the loss of a nitro-group under the influence of alkali, 2:4-dinitrobenzaldehydephenylhydrazone remains unchanged by similar treatment. To test the theory that this difference in behaviour is sterically due to the accumulation of atoms and atomic groups round the aldehydic carbon atom, 2:4-dinitroacetophenonephenylhydrazone, reddish-brown needles, m. p. 165—166°, has been pre-

pared from 2:4-dinitroacetophenone, an oil which is obtained by hydrolysing its oxime, yellow prisms, m. p. 124°, with warm 15% hydrochloric acid. The oxime is obtained in 20—30% yield by the action of amyl nitrite and sodium ethoxide on 2:4-dinitroethylbenzene, the main product of this reaction, however, being 5-nitro-2-methylindoxazen, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{CMe} \\ \text{O} \end{smallmatrix} \text{N}$, yellow crystals, m. p. 114°.

In accordance with the theory above, 2:4-dinitroacetophenone-phenylhydrazone is converted by treatment with cold aqueous-alcoholic sodium hydroxide into 6-nitro-1-phenyl-3-methylisindazole, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{NPh} \\ \text{CMe} \end{smallmatrix} \text{N}$, yellow spangles, m. p. 139—140°.

C. S.

Thienylquinolinecarboxylic Acid. MAX HARTMANN and ERNST WYBERT (*Helv. Chim. Acta*, 1919, **2**, 60—63).—2-2'-Thienylquinoline-4-carboxylic acid, $\text{C}_4\text{H}_3\text{S} \cdot \text{C}_9\text{H}_5\text{N} \cdot \text{CO}_2\text{H}$, yellow leaflets, m. p. 211°, is obtained by heating 2-thienyl methyl ketone, isatin, 28% potassium hydroxide solution and alcohol on the water-bath for three hours and acidifying the cooled solution with acetic acid. By repeated recrystallisation the acid is obtained in colourless crystals having the same m. p., but by solution in alkali and reprecipitation by acid the yellow modification is regenerated. The ethyl ester, colourless needles, has m. p. 83°. The salts of the acid are extremely soluble in water, forming solutions having a neutral reaction.

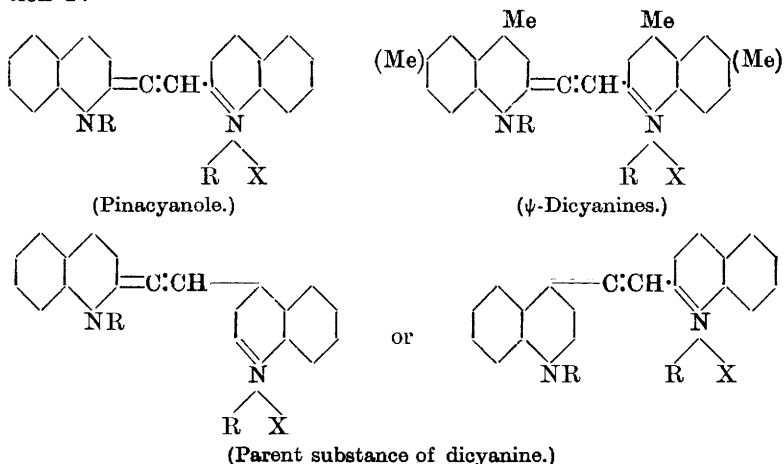
The acid resembles, but exceeds, 2-phenylquinoline-4-carboxylic acid in its antiphlogistic and analgesic action. When fed to an animal or when injected in the form of a soluble salt into the blood system it produces in the animal a violet-red colour and the urine acquires the colour of concentrated potassium permanganate solution. The colouring matter, which is very persistent and appears in almost all the internal organs, can be isolated from the urine and is obtained in small crystals (C=56·51; H=4·57; N=5·41; S=7·31%. Mol. wt. in freezing naphthalene=2207). The substance has pronounced acid properties, exhibits none of the colour reactions typical of thiophen, and cannot be produced from the thienylquinolinecarboxylic acid in the laboratory.

C. S.

Nitro-, Arylazo-, and Amino-glyoxalines. ROBERT GEORGE FARGHER and FRANK LEE PYMAN (*T.*, 1919, **115**, 217—260).

Quinocyanines (Pinacyanoles, Dicyanines). OTTO FISCHER (*J. pr. Chem.*, 1918, [ii], **98**, 204—232).—Little has hitherto been known of the blue cyanines which have been put on the market under the names pinacyanole chloride, dicyanine bromide, and ψ -dicyanine iodide, and are stated to be the best sensitisers in photography. Considerable light is now thrown on the conditions of their formation. For the production of pinacyanoles and of their homologues, the ψ -dicyanines obtained from 2:4-di- and 2:4:6-trimethylquinoline alkyl iodides, two quinoline molecules are necessary,

each containing a methyl group in position 2, by means of which the two molecules are united together. For the production of dicyanines are necessary two quinoline molecules, one containing a methyl group in position 2 and the other a methyl group in position 4:



In the formulæ $R = \text{Me}$ or Et and $X = \text{halogen}$.

The chromophore of the *isocyanines* (for example, ethyl-red) contains two, that of the *pinacyanoles* three, and that of the *dicyanines* four double linkings, which accounts for the deepening of the colours from violet-blue through blue to greenish-blue.

[With (Frl.) C. BAUER, (Frl.) P. MERKEL, and G. SCHEIBE].—The simplest pinacyanole, quinaldine-blue (formula given above), was prepared (Farbwerke vorm. Meister, Lucius & Brüning, D.R.-P. 172118) by boiling an alcoholic solution of quinaldine ethiodide, with or without quinoline ethiodide, with aqueous sodium hydroxide in the presence of formaldehyde. At first it was believed that two different blue pinacyanoles were formed, but it is now shown that only one is obtained, the quinoline ethiodide taking no part in the reaction. It is also shown that the presence of formaldehyde (or, as stated in the patent claim, of glyoxylic acid, iodoform or chloroform), although advantageous, is not essential, provided air or other oxidising agent, such as potassium ferricyanide or ammonium persulphate, is present. It is true that in the case of quinoline derivatives unsubstituted in position 4 the latter methods result chiefly in the production of *isocyanines*, but when position 4 is occupied by a methyl or phenyl group the product is chiefly the pinacyanole.

In addition to the iodide (quinaldine-blue), m. p. about $276-278^\circ$ (decomp.), the bromide, m. p. about $274-275^\circ$ (decomp.), chloride, m. p. about 263° (decomp.), picrate, decomp. about $250-260^\circ$, *platinichloride*, *aurichloride*, and *mercurichloride* are described, and also the additive compounds of the iodide and bromide respec-

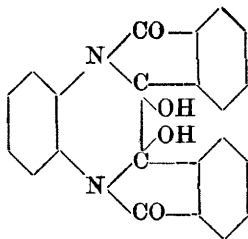
tively with bromine. Attempts to find evidence of the presence of a ruptured ring by testing for the presence of a secondary amine gave negative results. By oxidation with an excess of alkaline potassium ferricyanide solution, pinacyanole chloride yields 1-ethylquinolone.

Many attempts were made to convert ethyl-red and its homologues into pinacyanoles by means of formaldehyde, but the violet-blue substances obtained showed no similarity at all to the pinacyanoles.

By boiling an alcoholic solution of 2:4-dimethylquinoline ethiodide and potassium hydroxide ($\frac{1}{2}$ mol.) in a current of air a mixture of several colouring matters is produced, from which the ψ -dicyanine iodide, $C_{26}H_{27}N_2I$ (formula above), and the dicyanine iodide (formula above) have been isolated in the form of the corresponding bromides. When 4-phenyl-2-methylquinoline methiodide is similarly treated in methyl-alcoholic solution, no dicyanine is formed, but the ψ -dicyanine, 4:4'-diphenylpinacyanole iodide, $C_{34}H_{27}N_2I$, crystals containing CH_4O (*picrate*, almost black, crystalline powder), is obtained. A similar result is obtained in the case of 4-phenyl-2:6-dimethylquinoline methiodide, but 2:4:6-trimethylquinoline ethiodide, which again contains a methyl group in position 4, yields both the ψ -dicyanine iodide (chief product) and the dicyanine iodide. The former, $C_{28}H_{31}N_2I$, green prisms containing C_2H_6O , forms blue solutions which appear reddish-violet in thin layers (*picrate*, dark green leaflets), whilst the latter, $C_{28}H_{31}N_2I$, forms green needles (*picrate*, greenish-black needles; *bromide*, green needles).

The various classes of cyanines are differentiated by their absorption spectra. C. S.

Condensation of Aromatic *ortho*Diamines with Phthalic Anhydride. HANS LIEB (*Monatsh.*, 1918, 39, 873—895).—It has been shown by Edlbacher that diphtalyl-*o*-phenylenediamine, $C_6H_4N_2[(CO)_2C_6H_4]_2$, can be reduced by zinc dust and acetic acid to a substance, m. p. 275—277° (decomp.), which, at its melting point, passes into a red, crystalline product, $C_{22}H_{12}O_2N_2$, m. p. 278°. The present communication deals with the constitution of these substances, the elucidation of which in the first case is greatly hampered by the difficulty of eliminating solvent of crystallisation. The

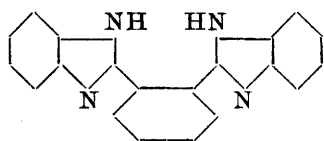


author, however, considers the material to be 1:2:3:4-dibenzoylene-1:2:3:4-tetrahydro-2:3-dihydroxyquinoxaline (annexed formula), whilst the substance, $C_{22}H_{12}O_2N_2$, is 1:2:3:4-dibenzoylene-1:4-dihydroquinoxaline. Similar substances may be obtained from phthalic anhydride and 1:2-naphthalenediamine.

Diphtalyl-o-phenylenediamine, m. p. 297°, is obtained in 45% yield by heating a mixture of phthalic anhydride and

o-phenylenediamine, and is reduced to 1:2:3:4-*dibenzoylene*-2:3-*dihydroxy*-1:2:3:4-*tetrahydroquinoxaline*, which separates from glacial acetic acid (+ $1\text{C}_2\text{H}_4\text{O}_2$) in yellow prisms, and from aqueous alcohol (+ H_2O) in indefinite, crystalline aggregates. The m. p. is not sharp, the substance becoming red at above 260° and yielding an intensely red, molten mass at $274\text{--}278^\circ$ with brisk evolution of gas. Attempts to prepare an acetyl or benzoyl derivative, an oxime or a hydrazone were unsuccessful, but the action of methyl sulphate yielded a monomethyl ether, $\text{C}_{23}\text{H}_{16}\text{O}_4\text{N}_2\cdot\text{H}_2\text{O}$, m. p. 190° , after softening and evolving gas from 170° . 1:2:3:4-*Dibenzoylene*-1:4-*dihydroquinoxaline* crystallises in intensely red needles, m. p. 278° ; it slowly dissolves in concentrated alcoholic potassium hydroxide, and the solution, on acidification, yields a substance which at $270\text{--}273^\circ$ is reconverted into the red product, but which, in spite of its close similarity, is not identical with the original material.

Attempts to prepare the red substance from biphtalyl and



o-phenylenediamine were not successful, the product obtained being *o*-phenylenedibenziminazole (annexed formula), colourless needles, m. p. 425° (decomp.), which was also prepared by condensing dihydrodiphtalyl with *o*-phenylenediamine or

from the amine and phthalic anhydride at 290° in a sealed tube. The corresponding acetyl and benzoyl derivatives have m. p.'s $198\text{--}199^\circ$ after softening at 195° and $229\text{--}230^\circ$ after softening at 225° respectively.

The following derivatives have been obtained from 1:2-naphthylenediamine: *diphtalyl*-1:2-*naphthylenediamine*, rhombohedra or hexagonal prisms, m. p. 282° , which on reduction gives the product, $\text{C}_{26}\text{H}_{16}\text{O}_4\text{N}_2$, m. p. $280\text{--}284^\circ$, with evolution of gas and formation of a red mass, and 1:2:3:4-*dibenzoylene*-1:4-*dihydro*-5:6-(7:8)-*benzquinoxaline*, red needles, m. p. $323\text{--}324^\circ$, after sintering at 321° . During the preparation of the first-named substance, 1:2-*naphthylenebenziminazole-o-carboxylic acid*, leaflets, m. p. $304\text{--}305^\circ$, is obtained as by-product; this is converted by acetic anhydride into *benzoylenenaphthiminazole*, $\text{C}_{18}\text{H}_{10}\text{ON}_2$, orange-yellow needles, m. p. 213° .
H. W.

Proteins. I. Preparation of Ovalbumin Solutions of well-defined Composition, and the Analytical Methods used.

S. P. L. SÖRENSEN [with MARGRETHE HÖYRUP] (*Compt. rend. trav. Lab. Carlsberg*, 1917, 12, 1—11, 12—67; *Zeitsch. physiol. Chem.*, 1918, 103, 1—14, 15—79).—The crystals of ovalbumin are prepared by the Hopkins and Pinkus' method, and after being recrystallised six times are free from ash, conalbumin, and mucoid. By means of a dialysing apparatus described in detail, solutions of ovalbumin may be completely freed from sulphate and almost entirely freed from ammonia. The content of water, ammonia,

and sulphuric acid in the crystals of ovalbumin is derived by the application of the "principle of proportionality," according to which, if an ovalbumin solution is precipitated by ammonium sulphate and the crystalline precipitate subsequently filtered off, and if weighed parts of the filtrate as well as of the precipitate with the adherent mother liquor are analysed, it is possible from the results of the analyses to draw certain conclusions regarding the composition of the precipitate on the presumption that the mother liquor surrounding the precipitate has the same composition as the filtrate.

H. W. B.

Proteins. II. Capacity of Ovalbumin to Combine with Acids or Bases. S. P. L. SÖRENSEN [with MARGRETHE HÖYRUP, JENNY HEMPEL, and S. PALITZSCH] (*Compt. rend. trav. Lab. Carlsberg*, 1917, **12**, 68—163; *Zeitsch. physiol. Chem.*, 1918, **103**, 104—210).—From theoretical considerations it is possible to calculate the hydrogen-ion concentration in an aqueous salt solution containing an excess of an acid or base corresponding with the salt. By an extension of the method, formulæ are deduced which permit of the calculation of the hydrogen-ion concentration of solutions of ampholytes containing small amounts of free acid, account being taken of the dissociation of the ampholyte into hydrogen- and ampholyte-anions and into hydroxyl and ampholyte cations respectively. The effect of the addition of salts is then considered, and it is found that at hydrogen-ion concentrations which are not in the neighbourhood of the isoelectric point of the ampholyte the capacity to combine with acids is (a) independent of the concentration of the ampholyte, (b) increased by increasing the concentration of the salt, (c) positive at hydrogen-ion concentrations superior to that corresponding with the isoelectric point of the ampholyte, and negative (that is, the ampholyte is combined with surplus base) at hydrogen-ion concentrations inferior to it. After testing the accuracy of these formulæ by application to solutions of amino-acids and salts, they are applied to solutions of ovalbumin, and it is found that the capacity of the ovalbumin to combine with acids is independent of the concentration of the ovalbumin at hydrogen-ion concentrations which are greater or smaller than that corresponding with the isoelectric point of the ovalbumin provided the concentration of ammonium sulphate is constant. It is further increased by increasing the concentration of the ammonium sulphate. At the isoelectric point the capacity of the ovalbumin to combine with acids is to some extent dependent on its concentration. By reference to a curve, the slight excess of sulphuric acid present in a solution of ovalbumin containing ammonium sulphate may be calculated, and also the method of its distribution between the two phases of the ovalbumin solution, namely, the dispersed phase consisting of hydrated ovalbumin and the external phase of ammonium sulphate and water. From these considerations the isoelectric point of ovalbumin is found to be at about 15.74×10^{-6} H. W. B.

Proteins. III. Composition and Properties of Ovalbumin Separated in Crystalline Form by means of Ammonium Sulphate. S. P. L. SÖRENSEN and MARGRETHE HÖYRUP (*Compt. rend. trav. Lab. Carlsberg*, 1917, **12**, 164—212; *Zeitsch. physiol. Chem.*, 1918, **103**, 211—266. Compare preceding abstracts).—By the application of the principle of proportionality, it is found that the crystals of ovalbumin contain water to the extent of about 0.22 gram of water per 1 gram of ovalbumin. The amount of water present is independent of the conditions of crystallisation (time and temperature of crystallisation, concentrations of ammonium sulphate, protein, and hydrogen ions). It is similarly found that if the crystallisation takes place at a hydrogen-ion concentration of about 13×10^{-6} , the crystals contain neither surplus sulphuric acid nor ammonia; at higher hydrogen-ion concentrations, the crystals contain surplus sulphuric acid, at lower concentrations they contain surplus ammonia. A consideration of the character of the crystallisation process leads the authors to the conclusion that the crystallisation of ovalbumin is simply the crystallisation of a supersaturated solution of a substance crystallising slowly and with difficulty.

In a postscript, it is announced that successful crystallisations of ovalbumin have been obtained by means of a mixture of ammonium and diammonium phosphates instead of ammonium sulphate. The crystals so obtained closely resemble those prepared in the usual manner.
H. W. B.

Proteins. IV. State of Equilibrium between Crystallised Ovalbumin and Surrounding Mother Liquor, and the Applicability of Gibbs's Phase Rule to such Systems. S. P. L. SÖRENSEN and MARGRETHE HÖYRUP (*Compt. rend. trav. Lab. Carlsberg*, 1917, **12**, 213—261; *Zeitsch. physiol. Chem.*, 1918, **103**, 267—323. Compare preceding abstracts).—The relations existing between crystallised ovalbumin and the surrounding mother liquor are in conformity with those associated with a heterogeneous system containing one solid phase, hydrated ovalbumin, and three other components, water, ammonia, and sulphuric acid. The system in all essential features is conformable to Gibbs' phase rule. At the equilibrium point, the content of ovalbumin in the mother liquor is smaller as the concentration of ammonium sulphate increases. The hydrogen-ion concentration at which the concentration of ovalbumin in the mother liquor is at a minimum corresponds with $p_H = 4.58$, and seems to be independent of the concentration of ammonium sulphate and the temperature of crystallisation. Similarly, the optimum temperature is at about 20° ; but little variation is observed between the limits of 12° and 29° .

The velocity of crystallisation increases with the concentration of ammonium sulphate, with the initial concentration of protein, and with the temperature of crystallisation.
H. W. B.

Proteins. V. Osmotic Pressure of Ovalbumin Solutions.

S. P. L. SÖRENSEN [with J. A. CHRISTIANSEN, MARGRETHE HÖYRUP, S. GOLDSCHMIDT, and S. PALITZSCH] (*Compt. rend. trav. Lab. Carlsberg*, 1918, **12**, 262—372. Compare preceding abstracts).—The osmometer used consists essentially of a collodion cap serving the purpose of a semi-permeable membrane and containing the ovalbumin solution employed as inner liquid, the outer liquid being an ammonium sulphate solution in diffusion equilibrium with the dispersion medium of the inner liquid. The osmotic pressure is measured by determination of the counter-pressure required to be exerted on the surface of the inner liquid to prevent a migration of the liquids through the membrane. On increasing the concentration of ammonium sulphate, the osmotic pressure of the ovalbumin is depressed. This result is explained by assuming that the increased amount of ammonium sulphate favours the condensation of two or more hydrated ovalbumin particles into a single particle by means of the bivalent sulphate group.

The osmotic pressure does not undergo any material alteration when the hydrogen-ion concentration is varied between 40×10^{-6} and 100×10^{-6} ; at higher concentrations, the pressure increases very slowly with the hydrogen-ion concentration, whilst at concentrations inferior to 40×10^{-6} , it increases rapidly as the concentration decreases. These results are also accounted for by the assumption of a condensation process promoted by the sulphate group.

From the various results which have been so far obtained, the number of nitrogen atoms contained in a single non-condensed ovalbumin particle is estimated at approximately 380; hence the molecular weight of anhydrous ovalbumin appears to be about 34,000. Taking into account the results obtained indicating the amount of sulphuric acid contained in the crystallised ovalbumin, the albumin crystals seem to consist normally of two albumin particles bound together by three molecules of sulphuric acid.

H. W. B.

Proteins of Cow's Colostrum. I. The Relation between the Euglobulin and ψ -Globulin of Cow's Colostrum.

HAROLD WARD DUDLEY and HERBERT ERNEST WOODMAN (*Biochem. J.*, 1918, **12**, 339—351).—The authors have studied the optical properties of euglobulin and ψ -globulin of cow's colostrum when dissolved in $N/2$ - and $N/4$ -sodium hydroxide, and also the optical properties of the amino-acids derived from the hydrolysis of "race-mised" colostrum euglobulin and ψ -globulin. The results obtained support the view that these two substances are structurally identical in so far as the protein portion of the molecule is concerned.

W. G.

Some Metallic Compounds of Hæmatoporphyrin.

JOHN ALEXANDER MILROY (*Biochem. J.*, 1918, **12**, 318—338).—The author has prepared the compounds of hæmatoporphyrin with zinc, cadmium, nickel, cobalt, iron, copper, tin, and lead, has described their absorption spectra, and determined their resistance to the

action of mineral acids and the resistance of the absorption bands of the pigments to dilution.

The stannous compound may be prepared directly from blood or hæmatin, and on this is based a delicate test for the detection of traces of blood pigment. The stained tissue, where blood is suspected, is boiled with a little glacial acetic acid in a small test-tube. To the boiling solution, three drops of 2*M*-stannous chloride solution are added, and the solution is boiled for one minute. After filtering off the precipitate formed, the absorption bands of acid hæmatoporphyrin can easily be seen. A small quantity of solid sodium acetate is then added, and the solution is again boiled. The fluid, which is now bright red, is cooled and filtered, and the filtrate shows the two characteristic absorption bands of the stannous derivative. A method is given for extracting the blood pigment with phenol prior to this examination, and it is claimed that, by this means, it is possible to detect blood pigment at a dilution of $10^{-6} \times M/5$.
W. G.

Pyrrole Reaction of the true Nucleic Acids. R. FEULGEN (*Zeitsch. physiol. Chem.*, 1918, **104**, 1).—A pine shaving moistened with concentrated hydrochloric acid is coloured carmine-red by the vapours obtained by heating a dry mixture of sodium nucleate and ammonium chloride; the reaction is not shown by sodium nucleate alone. Since furan derivatives are readily converted into derivatives of pyrrole by dry distillation with ammonium salts, the author regards the reaction as a confirmation of his theory (A., 1914, i, 1098; 1918, i, 85) that the carbohydrate group of the true nucleic acids belongs to the furan type.
H. W.

Mutarotation of Gelatin and its Significance in Gelatinisation. C. R. SMITH (*J. Amer. Chem. Soc.*, 1919, **41**, 135—150).—In solution, gelatin exhibits mutarotation, and a study of the influence of changes of temperature on this mutarotation shows that in aqueous solution two forms of gelatin probably exist, one, termed the sol form *A*, stable above 33—35°, and the other, called the gel form *B*, stable below 15°. Between these temperatures, the two forms exist in equilibrium, and the mutarotation appears to be due to the transformation of the one form into the other by a reaction reversible with the temperature. This reaction is apparently bimolecular, that is, of the type to be expected if two molecular or equivalent weights of form *A* combine to form one molecular weight of form *B*. The relationship between the percentage quantities of the two forms when equilibrium is established at any given temperature between 17° and 33° seems to be represented by the equation $(a-x)^2/x=K$, in which *a* is the difference (about 1.2) between the rotations produced by 1 gram of gelatin per 100 c.c. in a tube 100 mm. long at 33—35° and at 17°, *x* is the difference between the rotations at 33—35° and at the given temperature, and *K* is a constant. Increase in levorotation, indicating increasing formation of the gel form *B*, follows closely increase in viscosity.

A definite proportion of form *B* is necessary to form a jelly of standard viscosity, and this proportion, slightly increased as concentration increases, produces the standard viscosity in gelatin solutions of much higher concentrations. Maximum gelatinisation temperatures or melting points approach the limiting value, 33—35°, as the concentration of gelatin increases. At these maximum temperatures, gelatinisation is produced by the presence of a certain definite minimum proportion of form *B* required for the formation of a jelly; above 35°, gelatinisation does not take place at any concentration.

The existence of two forms of gelatin, on which gelatinisation of the solutions is dependent, is confirmed by the behaviour of such solutions with alcohol, which at temperatures below 30° either precipitates the gelatin or renders the solutions opalescent if present to the extent of 15%; if the concentration of the gelatin is high, alcohol precipitates an opalescent jelly. Above 35°, the precipitation requires far larger proportions of alcohol (45—50%), unless a comparatively large amount of an electrolyte is also added. Further confirmation is afforded by the results of measurements of osmotic pressure (compare Moore and Roaf, A., 1907, ii, 73), viscosity (von Schroeder, A., 1903, ii, 721), and "gold numbers" (Menz, A., 1909, i, 343).

Gelatin sols dried at above 35° and gels dried at below 15° give different solid forms, and whilst the solid gelatin thus obtained may or may not be in the form in which it exists in the material from which it is prepared, there is some indication that the solid gelatin prepared by drying sols above 35° is the form existing in the sols.

T. H. P.

Pepsin. I. Chemical Changes in the Purification of Pepsin. LEWIS DAVIS and HARVEY M. MERKER (*J. Amer. Chem. Soc.*, 1919, **41**, 221—228).—The purification of commercial pepsin by fractional precipitation, salting-out, filtration, and dialysis is accompanied by gradual elimination of the secondary protein derivatives, including amino-acids, the purified samples tending more and more to approach the proteins in character as the proteolytic activity increases; the proportion of material coagulable by heat also increases. The fact that the most active samples respond strongly to Molisch's test indicates the possibility that the pure enzyme may be a conjugated protein, probably a gluco-protein. The proportion of mineral matter present also diminishes continuously as purification proceeds; the sulphur and calcium appear, however, to be unaffected, although the phosphorus content shows a marked decrease and chlorides are apparently eliminated entirely. Other than the increase resulting from removal of non-nitrogenous impurities, there is little apparent change in the proportion of total nitrogen.

The diminution in the α -amino-acid content is almost proportional to the increase in proteolytic activity, and the small amount of α -amino-acid in the most active sample, which exhibits an almost neutral reaction, appears to correspond with lysine. It seems probable that the concentration of hydrogen ions in solutions of the

pure enzyme, could this be obtained, would be comparable with the low values given by other proteins.

The optical activities of the enzymes of different degrees of purity were measured, but the same values were obtained with pepsins showing different proteolytic activities. The rennetic activities correspond closely with the proteolytic activities.

T. H. P.

A Delicate Method of Determining Invert Activity. C. K. WATANABE and V. C. MYERS (*Proc. Soc. Exp. Biol. Med.*, 1918, **15**, 142—143; from *Physiol. Abstr.*, 1919, **3**, 502).—The method is similar to that advocated by Myers and Killian (compare A., 1917, i, 369) for measuring diastatic activity, but in this case sucrose solution is substituted for the solution of soluble starch or glycogen.

W. G.

Influence of Hydrogen-ion Concentration on the Enzymic Activity of Three Typical Amylases. H. C. SHERMAN, A. W. THOMAS, and M. E. BALDWIN (*J. Amer. Chem. Soc.*, 1919, **41**, 231—235).—The enzymes examined were the amylases of pancreas, malt, and *Aspergillus oryzae*, representing the starch-splitting enzymes of the higher animals, higher plants, and fungi respectively. Experiments were made to determine as definitely as possible the hydrogen-ion concentrations which induce optimal activity of the pancreatic and fungus amylases, and to establish for each of the three amylases the limits of hydrogen-ion concentration within which any enzymic activity is shown and the form of the curve representing the activities at all concentrations of the hydrogen ion between these limits. The experimental methods used were those previously described (A., 1915, i, 183), except that greater precautions were taken to prevent any action of light during the enzymic actions, and that, in measuring the hydrogen-ion concentration by the electrometric method, the current of hydrogen was replaced by a Clark cell and a rocking electrode.

The results of Sherman and Thomas (*loc. cit.*) on the optimum hydrogen-ion concentration for malt amylase were confirmed and that for pancreatic amylase more sharply defined; that for the maltase of *Aspergillus oryzae* is closer to the value for malt amylase than to that for the pancreatic enzyme. The latter is active for values of P_H 4—10, the optimal activity being at about 7; the solutions commonly considered neutral show under similar conditions the value 5·8 for P_H . Malt amylase is active for P_H = 2·5—9, the optimal activity being at 4·4—4·5, whilst with the *Aspergillus* enzyme the limits of P_H are 2·6 and 8 and the optimum 4·8. The influence of the concentration of the electrolyte, as distinguished from the concentration of the hydrogen ion alone, appears to be greatest with pancreatic amylase and least with the amylase of *Aspergillus oryzae*.

T. H. P.

Effect of Neutral Salts on the Activity of Ptyalin. ELBERT W. ROCKWOOD (*J. Amer. Chem. Soc.*, 1919, **41**, 228—230).—The

methods used in this investigation were essentially those previously described (A., 1917, i, 358; 1918, i, 274). Ammonium chloride and nitrate, and, to a less extent, the sulphate and thiocyanate, enhance the hydrolytic action of ptyalin on starch. The effects of the ammonium salts of organic acids are much smaller; the acetate, but not the oxalate, shows some power as an auxo-amylase, whilst the tartrate exerts a slight stimulating action. Ammonium chloride and bromide produce marked increase in the amount of starch hydrolysed; the quantity of reducing products being the same in each case; the fluoride inhibits the action. Similar results are obtained with the sodium haloids. The effect of sodium chloride is not altered by changing the cation to potassium or calcium, so that the action of a salt is a function, not of the cation, but of the anion. The trivalent cations were not tested, owing to the coagulating effect of their soluble salts on colloids.

Tests made by means of Nessler solution at intervals during the action of ptyalin on starch in presence of an ammonium salt show that the ammonium ion is not destroyed during the digestion.

T. H. P.

Photochemical Effect of certain Fluorescent Substances on Rennin. JANET H. CLARK (*Amer. J. Physiol.*, 1918, **47**, 251—264; from *Physiol. Abstr.*, 1919, **3**, 502).—The inhibition of rennin by light is attributed to the formation of toxic substances as a result of photochemical action. This may be accompanied by fluorescence, and fluorescence may or may not be accompanied by the formation of toxic substances. Free halogens are the toxic substances in the experiments described with eosin and erythrosin.

W. G.

Simple Method of Making *p*-Arsanilic Acid. PHILIP ADOLPH KOBER and WALTER S. DAVIS (*Proc. Soc. exp. Biol. Med.*, New York, 1918, **16**, 13—15).—1000 C.c. of crude 75% arsenic acid are concentrated to about 100 c.c. by heating for twelve to fifteen hours in an open beaker in an oil-bath at 120—140°. After cooling, the acid is slowly added, with vigorous stirring, to 1400 c.c. of dry aniline, at or below 0°. The mixture becomes viscous, then granular, and is finely ground. 200 Grams of it are heated in a flask and stirred until the powder melts; it is then heated for one and a-half hours at 160—170° and one hour at 180—183°, under a reflux condenser. After cooling, 450 c.c. of 3*N*-hydrochloric acid are added, the aniline is separated off, the solution is shaken with 15—20 grams of kaolin or infusorial earth, and filtered with aid of suction. To the clear filtrate, 100 c.c. of 6*N*-hydrochloric acid are added, and then, on an aliquot portion, the further amount of hydrochloric acid is determined by trial, which will give the maximum crystallisation on keeping. This, added to the main bulk, yields 30% of crystalline primary arsanilic acid, without any secondary acid. The usual mistake in the laboratory is to employ too much aniline and too high a temperature.

G. B.

Method of Preparing Pure Dihydrochloride of Diamino-dihydroxyarsenobenzene [Salvarsan]. PHILIP ADOLPH KOBER (*Proc. Soc. exp. Biol. Med., New York*, 1918, **16**, 23—24).—The author dislikes the precipitation of the dihydrochloride from methyl alcohol by ether, and prefers the mass action of strong hydrochloric acid in aqueous solution. The alkaline solution of the base is slightly acidified with hydrochloric acid, and the solution is poured slowly, with vigorous stirring, at a low temperature into hydrochloric acid (1 in 1, or more dilute). This obviates coagulation of the flocculated particles. G. B.

Halogenation. XVII. Action of Halogens on the Grignard Reagent and Replacement of Halogen Atoms by one another. RASIK LAL DATTA and HARAPARBUTTY KUMAR MITTER (*J. Amer. Chem. Soc.*, 1919, **41**, 287—292).—Few investigations have been made on the action of halogens on the Grignard reagent. The authors find that one halogen is, in general, able to displace other halogens from the Grignard reagent with the production of the corresponding haloid derivatives, the yield of the latter being greatly influenced by the nature of the halogen and by the experimental conditions; the reaction is sometimes accompanied by secondary reactions due to the union of the Grignard residues.

When iodine is added to magnesium phenyl bromide, the resultant products are iodobenzene in 25—30% yield, benzene in 30—40% yield, and a small proportion of diphenyl, but addition of magnesium phenyl bromide to ethereal iodine solution gives phenyl iodide in 90% yield. By the action of iodine on magnesium phenyl iodide, iodobenzene, benzene, and diphenyl are formed, the last constituting the main product. The action of iodine on magnesium *o*-tolyl bromide gives *o*-iodotoluene in 80% yield. From *m*-bromotoluene, *m*-iodotoluene is similarly obtained in 76% yield, as well as a little unchanged *m*-bromotoluene; from *p*-bromotoluene, in addition to a little unchanged substance, *p*-iodotoluene is formed in 74% yield. By the action of iodine on magnesium ethyl iodide, ethyl iodide in low yield is obtained.

Similarly, in the action of bromine on magnesium phenyl iodide, benzene and bromobenzene are the principal products, the yield of the latter being 30—40%; a small proportion of diphenyl is also obtained. From magnesium phenyl bromide, bromobenzene is obtained in 30—40% yield. By the action of bromine on magnesium ethyl iodide, ethyl bromide is formed, and from magnesium *n*-propyl iodide, propyl bromide is formed in 30—40% yield.

The action of chlorine on magnesium phenyl bromide gives a product which explodes with great violence when shaken. From *p*-bromotoluene, *p*-chlorotoluene is obtained in 20% yield.

T. H. P.

Physiological Chemistry.

The Coagulation of Blood. MARIO CHIO (*Arch. Farm. speriment.*, 1918, **25**, 175—192, 193—212; from *Chem. Zentr.*, 1918, ii, 1048).—The behaviour towards hydrochloric acid and carbon dioxide (*A.*, 1917, i, 672) varies with the season of the year in such a manner that, during the warmer months, smaller concentrations of hydrochloric acid are sufficient to prevent the coagulation of the salt plasma, whilst, on the other hand, higher tensions of carbon dioxide are necessary. It is advisable, although not absolutely necessary, to perform the experiments at constant temperature. New experiments have shown that a displacement of the chemical equilibrium in dilute salt plasma occurs, which is shown by an increase in alkalinity. Hydrolysis of fatty matter must, among other influences, be a cause and consequence. Hydrolytic fission of alkali soaps liberates fatty acids, which yield calcium soaps in the presence of soluble and dissociable calcium salts. Changes therefore occur in the condition of certain colloids, which result first in the formation of gels and subsequently in contraction, owing to diminution in the irrigation of the lipid-albumin complexes. Increase in the tension of carbon dioxide diminishes the rate of this phenomenon. The coagulation of blood may be explained by the formation of calcium soaps by a process which can be limited or prevented by suitable adjustment of the carbon dioxide tension both outside and within the organism. H. W.

Proteolytic Relationships in the Serum of the Horse and Ox. S. G. HEDIN (*Zeitsch. physiol. Chem.*, 1918, **104**, 11—47).—A continuation of the work of Hedin and Masai (*A.*, 1918, i, 90). The chief results may be summarised as follows: The serum shows itself either completely inactive or very slightly active towards casein, but undoubtedly capable of breaking down peptone when tested by the tannic acid method. If the serum is fractionated with ammonium sulphate, the globulin fraction, precipitated by about one-third saturation, contains primary and secondary proteases, and thus causes fission of casein and peptone. The first type of activity appears to be lost if the serum is heated at 56° during thirty minutes, whereas the second type persists in a greatly lessened degree. The albumin fraction precipitated between half and full saturation contains practically only secondary proteases, which are active towards peptone but not noticeably towards casein; it contains also substances which inhibit the activity of pancreas trypsin as well as of the primary proteases of the globulin fraction. The power of these inhibiting substances is destroyed or weakened by treating the albumin with chloroform or ether; if, however, they have already acted on the enzyme, subsequent treatment with chloroform is ineffective. H. W.

The Increase in Nitrogen Metabolism of the Dog, following the Administration of Desiccated Thyroid Gland.

ALICE ROHDE and MABEL STOCKHOLM (*J. Biol. Chem.*, 1919, **37**, 305—316).—Nitrogen elimination in the dog receiving only sugar solutions may be increased approximately 50% by the administration, during a five- to seven-day period, of commercial desiccated thyroid gland in doses of 0.10—0.15 gram per kilo. of body weight.

W. G.

The Acid-Base Balance in Animal Nutrition. I. The Effect of certain Organic and Mineral Acids on the Growth, Well-being, and Reproduction of Swine.

ALVIN R. LAMB and JOHN M. EVVARD (*J. Biol. Chem.*, 1919, **37**, 317—328).—With the view of testing the ability of swine to metabolise successfully the lactic and acetic acids of silage, four lots of two pigs each, all from the same litter, were fed with equal amounts of a good basal ration consisting of ground corn 80%, meat meal tankage 15%, standard wheat middlings 5%. One lot served as a control and the other three received in addition, respectively, sulphuric, lactic, and acetic acids in amounts increasing gradually up to 500 c.c. of *N*-acid per pig per day during 150 days. The three acid-fed lots grew practically as rapidly as the control, and remained in equally good condition. The organic acids seemed to be completely oxidised, and the sulphuric acid was neutralised without apparent harm or significant effect on growth. An examination of the blood at the end of the experiment showed that neither the organic nor mineral acids disturbed the reaction of the blood.

The two pigs fed with sulphuric acid were continued on the same ration for four to six months longer, and successfully produced young, but either the excessive amount of acid fed or some other factor prevented the successful rearing of the young.

W. G.

The Acid-Base Balance in Animal Nutrition. II. Metabolism Studies on the Effect of certain Organic and Mineral Acids on Swine.

ALVIN R. LAMB and JOHN M. EVVARD (*J. Biol. Chem.*, 1919, **37**, 329—342. Compare preceding abstract).—Metabolism studies on a growing pig fed on a ration containing a liberal allowance of calcium show that the animal apparently oxidised the organic acids (lactic and acetic) completely with no increase in urinary ammonia, and that the acids seemed to bring about a slightly increased retention of calcium. On the same basal ration plus 300 c.c. of *N*-sulphuric acid per day, 61% of the acid ingested was neutralised by means of ammonia, and 4.6% was accounted for by extra urinary acidity. On another basal ration very low in calcium, extra ammonia excretion accounted for 76% of the acid fed, and extra urinary acidity for 10%. On neither ration did the mineral acid cause a significant loss of calcium, nor did it interfere with the storage of protein.

W. G.

The Mechanism of the Action of Fats in the Utilisation and Assimilation of Proteins.

F. MAIGNON (*Compt. rend.*, 1919, **168**, 474—476. Compare A., 1918, i, 416).—The author con-

siders that the fats exercise a favourable action on the assimilation of albumin by intervening in the synthetic reconstitution of the proteins, and that in this action not only the glycerol portion of the fat molecule exercises an influence as already shown by Mailard, but also the fatty acid portion. Thus the fatty acids may combine with the amino-acid nucleus of a protein in formation and permit of the building up of a molecule, which it would not have been possible to obtain simply with the amino-acids available and without the assistance of the fats.

W. G.

A Method of Expressing Numerically the Growth-promoting Value of Proteins. THOMAS B. OSBORNE, LAFAYETTE B. MENDEL, and EDNA L. FERRY (*J. Biol. Chem.*, 1919, **37**, 223—229).—From feeding experiments with rats in which the proportion of protein in the food was so restricted that the protein factor alone determined the rate of growth, the authors determined, within limits, the concentration which promoted the greatest gain of body weight relative to the protein ingested by supplying foods containing different percentages of protein. The results indicate, in the first place, the necessity for employing a large number of animals. When an animal is restricted to such a quantity of protein that a maximum gain of body weight is made per unit of protein eaten, it grows at less than the normal rate. Economy in nutrition during growth depends on a correct adjustment between the proportion of protein and the total energy supplied, the optimum of protein being determined not only by the absolute amount furnished, but also by its quality.

W. G.

Accessory Factors in the Nutrition of the Rat. ARTHUR HARDEN and SYLVESTER SOLOMON ZILVA (*Biochem. J.*, 1918, **12**, 408—415).—An antiscorbutic does not fulfil the physiological function of the fat-soluble *A* when it replaces it in the diet of the rat. The authors confirm the observation of McCollum and co-workers and of Drummond that by depriving rats of the antineuritic factor a dietetic deficiency is brought about, as a result of which a fatal termination ensues if the diet is not rectified in time. Rats subsisting on a diet containing the antiscorbutic factor as well as the water-soluble and fat-soluble *A* factors grow better than rats from the diet of which the antiscorbutic factor is absent.

W. G.

Antiscorbutic Properties of Concentrated Fruit Juices. ARTHUR HARDEN and ROBERT ROBISON (*J. Army Med. Corps*, 1919, **32**, 48—56).—Orange-juice, evaporated at 40° under reduced pressure, gives a solid residue in which the antiscorbutic principle is still largely intact and remains so in a dry atmosphere at the ordinary temperature for six months. Apple jelly prepared in a Kestner evaporator also possesses antiscorbutic properties in a high degree, but is inferior to orange juice.

G. B.

Dietary Properties of the Pea (*Vicia sativa*). E. V. MCCOLLUM, N. SIMMONDS, and H. T. PARSONS (*J. Biol. Chem.*, 1919, **37**, 287—301).—Pea proteins are of very poor quality when

fed as the sole source of nitrogen. Casein and zein supplement the deficiencies of the pea proteins, but gelatin and lactalbumin do not. There is an indication of the presence in peas of some substance or substances which prove injurious when taken in large amounts, but the toxicity, if there be any, is but slight and only manifests itself when diets extremely rich in peas are persisted in over a long period.

From the failure of lactalbumin to supplement the proteins of the pea, or to induce growth when fed in the amounts used in the experiments described, the authors tentatively conclude that lactalbumin is either an incomplete protein or a poorly constituted one.

W. G.

Zinc, a Cellular Constituent of the Animal Organism. Its Presence and Rôle in the Venom of Serpents.

C. DELEZENNE (*Ann. Inst. Pasteur*, 1919, **33**, 68—136).—Of the zinc occurring in the blood of animals, the major portion is found in the leucocytes, a little in the red corpuscles, and practically none in the plasma. An examination of the different organs of a number of animals of different species shows that zinc is a constant constituent of all animal cells. In the venom of serpents it is present to the extent of 0.31—0.56% in the venom of Colubrids and 0.11—0.23% in that of Viperides, and is present, combined with organic constituents, in such a manner as not to be precipitated by hydrogen sulphide or separated by dialysis even in the presence of hydrochloric acid. It is probably combined with a proteose rich in sulphur, since the sulphur and zinc contents of the different venoms examined varied very closely in the same direction. The proportion of zinc present in the venoms was found to vary inversely with the proteolytic and coagulating properties of the venoms. On the other hand, the zinc content was found to run parallel with the nucleolytic activity and the diastatic activity, which gives rise to hæmolysis, venoms with high zinc content showing the greatest activity in these two directions. In this connexion it should be noted that in mammals it was found that those organs which were richest in phosphatides and nucleic acids had the highest zinc contents.

W. G.

Behaviour of the Kidneys towards some Isomeric Sugars (Dextrose, Lævulose, Galactose, Mannose, and Sucrose, Maltose, Lactose).

H. J. HAMBURGER and R. BRINKMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 548—561).—When Ringer's solution containing dextrose is passed through the kidneys (of frogs), this sugar is retained by the glomerulus membrane, whereas lævulose and mannose are allowed to pass entirely and galactose to a large extent. Sucrose, maltose, and lactose also pass through this membrane, the last perfectly; the membrane is also permeable to raffinose.

T. H. P.

The Physicochemical State of the Proteins in Cow's Milk.

LEROY S. PALMER and ROBERT G. SCOTT (*J. Biol. Chem.*, 1919, **37**, 271—284).—Samples of fresh skim-milk, skim-milk preserved either with 5% of chloroform or 0.05% of formaldehyde, and of the lactic acid whey from fresh skim-milk were filtered, under pressure, through Pasteur-Chamberland tubes, and in the filtrate the total protein, as precipitated by Almen's tannic acid reagent, and the non-protein nitrogen were determined. The amount of non-casein protein recovered in the filtrate did not in any case exceed 10% of the non-casein protein in the original milk, and in most cases was considerably less than this figure. There was also only a partial recovery of the non-protein nitrogen of the original milk in the experiments with milk preserved with chloroform and formaldehyde. These results differ widely from those of Van Slyke and Bosworth (compare A., 1915, i, 192). The authors consider that it is fallacious to draw conclusions regarding the true state of solution of non-casein proteins of milk based on filtration studies of this character, since there is considerable variation in size of the pores of different Pasteur-Chamberland filters. W. G.

The State of Proteins in Cow's Milk.

L. L. VAN SLYKE and A. W. BOSWORTH (*J. Biol. Chem.*, 1919, **37**, 285—286. Compare A., 1915, i, 192).—A reply to Palmer and Scott (compare preceding abstract). W. G.

Creatinuria and Acidosis.

W. DENIS and A. S. MINOT (*J. Biol. Chem.*, 1919, **37**, 245—252).—Feeding experiments carried out with two normal boys, four women suffering from hyperthyroidism, and two normal women did not demonstrate any definite connexion between changes in acid-base equilibrium and creatine excretion. W. G.

Chemistry of Vegetable Physiology and Agriculture.

The Effect of Acids on the Growth of *Bacillus coli*.

FRANK JOHN SADLER WYETH (*Biochem. J.*, 1918, **12**, 382—401).—All strains of *Bacillus coli*, whether of human or bovine origin, behave similarly when exposed to similar conditions. The degree of acidity of the final reaction produced by a culture of *B. coli* cannot be used for diagnostic purposes, the value not being a "physiological constant," but dependent on (a) the initial hydrogen-ion concentration of the medium in which fermentation occurs; (b) the composition of the medium, especially the degree to which it is "buffered"; (c) the nature of the acid used to produce the initial reaction of the medium. When the amount of acid added is insufficient completely to inhibit the fermentation

of *B. coli* therein, a definite latency of growth results, the latency increasing with the amount of acid initially added. Each acid has its own specific effect in inhibiting the growth of *B. coli* in a given medium, the inhibiting effect being greater as the acid is more highly dissociated. For a mixture of any given medium and acid, there appears to be a definite critical point, beyond which the slightest rise in the degree of acidity results in a complete inhibition of the growth of *B. coli*.
W. G.

Effect of Carbon Disulphide and Toluene on Nitrogen Fixing and Nitrifying Organisms. P. L. GAINNEY (*J. Agric. Res.*, 1918, 15, 601—614).—Carbon disulphide and toluene, if applied to soils in sufficient quantity, will destroy *Azotobacter* and check the accumulation of nitrates, and possibly will destroy nitrifying organisms. The amounts of these two antiseptics necessary to produce this effect vary widely with the conditions, being affected particularly by the moisture content of the soil, diminishing as the latter increases. Providing that sufficient antiseptic is added to have any effect on *Azotobacter*, they are usually completely destroyed, but, on the other hand, there is a great difference in the amount necessary to destroy nitrifying organisms and that necessary to check their activity. Unless nitrification has been checked, there is no appreciable accumulation of ammonia following the treatment with these antiseptics.

There are nitrogen-fixing organisms other than *Azotobacter* present in soils, which are not destroyed by the addition of 10 c.c. of carbon disulphide or toluene to 100 grams of soil, even when the moisture content of the soil is high.
W. G.

Production of Citric Acid by *Sterigmatocystis nigr* [*Aspergillus niger*]. MARIN MOLLIARD (*Compt. rend.*, 1919, 168, 360—363).—In culture solutions containing insufficient quantities of nitrogen and mineral salts for the sugar present, *Aspergillus niger* produces citric rather than oxalic acid, the amount increasing gradually at first, and then considerably between the eighth and tenth days, after which it remains almost constant. Citric acid is noticeable from the very first, but oxalic acid only appears towards the end of the second day, just at the time when the conidiæ commence to be formed, its amount only increasing very slowly.
W. G.

Course of the Formation of Diastase by *Aspergillus niger*. F. A. F. C. WENT (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, 21, 479—493).—*Aspergillus niger* was grown in the dark at $24 \pm 0.5^\circ$ in a culture solution containing 5% of dextrose, 0.5% of ammonium nitrate, 0.1% of potassium phosphate, and 0.05% of magnesium sulphate in glass flasks, the amount of diastase present in the liquid and in the fungus mass being determined at first daily and later every two, three, or more days. The method of determination consisted in ascertaining the length of time necessary

for the complete disappearance of the starch from a starch solution of definite strength mixed with the enzyme solution. The tests were made with a solution containing 0.0625 gram of iodine and 0.0625 gram of potassium iodide to 100 grams of water, 1 c.c. of this being found to give a distinct blue coloration with 0.001 gram of soluble starch, or a definite reddish-violet coloration with 0.0002 gram, in 10 c.c. of water.

During the first days after germination of the mould spores with which the culture liquid was inoculated, a great quantity of diastase is formed in the mycelium, this being accompanied by destruction of the enzyme, which is at first negligible in comparison with the formation, but soon makes itself so evident that the total quantity of diastase quickly decreases from the maximum reached about five days after the commencement of germination. Never more than a very small part of the total amount of the enzyme occurring in the mycelium passes into the nutrient solution, this being perhaps derived partly from dead cells.

T. H. P.

Occurrence of Iodine in Plants. E. WINTERSTEIN (*Zeitsch. physiol. Chem.*, 1918, **104**, 54—58).—The author has examined a considerable number of plants in respect of iodine content. The method employed consisted in ashing the plant in an alkaline condition and treatment of the residual mixture of salts with 95% alcohol, in which any iodides are soluble. The aqueous solution of the extract was treated with a solution of nitrosylsulphuric acid in concentrated sulphuric acid in the presence of chloroform, in which any liberated iodine dissolved to a red solution. Test experiments showed that 0.04 mg. of added iodine could be detected in 10 grams of spinach by this method.

Minute amounts of iodine are shown to occur in *Beta vulgaris*, *Solanum tuberosum*, *Apium graveolens*, *Lactuca sativa*, and *Daucus carota*. Iodine could not be detected in the fruit, seeds, tubers, or leaves of *Taxus baccata*, *Pinus silvestris*, *P. cembra*, *Abies pectinata*, *Zea Mays*, *Oryza sativa*, *Avena sativa*, *Hordeum sativum*, *Secale cereale*, *Triticum sativum*, *Allium cepa*, *Fagus sylvatica*, *Castanea vesca*, *Cannabis sativa*, *Urtica dioica*, *Polygonum fagopyrum*, *Spinacea oleracea*, *Lepidium sativum*, *Ribes grossularia*, *Pirus malus*, *P. communis*, *Prunus cerasus*, *Lupinus albus*, *L. angustifolius*, *Trifolium pratense*, *Vicia sativa*, *Pisum sativum*, *Soja hispida*, *Phaseolus vulgaris*, *Vitis vinifera*, *Stachys tuberifera*, *Curcubita pepo*, or *Aesculus hippocastanum*, or in the following fungi: *Cantharellus cibarius*, *Boletus edulis*, *Agaricus campestris*.

Iodine could not be detected in eight samples of milk, in five varieties of cheese, or in cow's urine.

H. W.

Chemical Composition of *Agave americana*, L. The Chemistry of Succulent Plants in General. JULIUS ZELLNER (*Zeitsch. physiol. Chem.*, 1918, **104**, 2—10).—The leaves of *Agave americana*, L., have been submitted to chemical examination along

the usual lines. The fresh leaves are remarkable for their high water content. For examination, the air-dried material was taken. The light petroleum extract (1·03%) contained fat, chlorophyll, and wax; the ethereal extract (0·74%) consisted of waxy matter. The aqueous extract (50·75%) was composed of amorphous carbohydrates (12·00%), sugar (calculated as dextrose, 12·68%), malic acid (about 8%), free acid (as H ions, 0·02%), ash (7·54%), other matter, such as small amounts of peptones, amino-acids, etc. (about 10%). The portion insoluble in indifferent solvents contained crude cellulose, including bast fibres (17·85%), pentosans (7·44%), methylpentosans (1·01%), pectin, hemicelluloses, oxalate (about 13%), mineral matter (4·82%), crude protein (3·25%).

The results are compared with those obtained from the examination of other succulent plants so far as the data are available. The high content of water-soluble substance, of calcium malate, of pectinous matter, and probably of sugar appears to be characteristic of the class, but it is not possible at present to decide whether the poverty in nitrogen and iron is a general feature. Further, it would appear that a volatile substance, probably an aldehyde, is frequently present in this class of plant.

H. W.

Is Selenium Present in the Vegetable and Animal Organism? R. FRITSCH (*Zeitsch. physiol. Chem.*, 1918, 104, 59—64).—According to Gassmann (A., 1916, i, 772; 1917, ii, 540), selenium is to be regarded as a definite constituent of the human, vegetable, and animal organisms. The author, however, considers that the methods on which Gassmann relies cannot give trustworthy results. He has therefore examined the question further, and has been unable to detect the presence of selenium in thirty-five samples of spinach, clover, corn, potatoes, or bones. The method adopted consisted of ashing the plant in the presence of sodium carbonate and sodium nitrate, and finally obtaining any selenium present as a solution of selenious acid in concentrated sulphuric acid; in this solution, the presence of selenium is detected by the green to bluish-green coloration with codeine, or the intense yellow coloration with colchicine. Test experiments showed that 2—0·5 mg. of selenious acid could be detected in 30—50 grams of plant material in this manner.

Selenium does not appear to be present in urine or bones.

H. W.

The Microchemical Detection and the Distribution of Soluble Oxalates in the Vegetable Kingdom. H. MOLISCH (*Flora*, 1918, 11—12, 60—70; from *Physiol. Abstr.*, 1919, 3, 540).—The methods employed by the author to ascertain the presence of soluble oxalates in plants were precipitation with (1) saturated alcoholic sodium hydroxide; (2) saturated alcoholic potassium hydroxide; (3) lead acetate; (4) barium chloride. Two hundred and forty plant species were examined. Soluble oxalates were found frequently in the phanerogams, and the following families

contained large quantities: Polygonaceæ, Chenopodiaceæ, Amarantaceæ, Aizoaceæ, Begoniaceæ, Milostomaceæ, Oxalideæ, Cannaceæ, and Marantaceæ.

W. G.

Spectrographic Study of the Ashes of Marine Plants.

EUGÈNE CORNEC (*Compt. rend.*, 1919, **168**, 513—514).—From a spectrographic study of the ashes of *Laminaria*, the presence of the following elements was shown: Group I, silver, arsenic, cobalt, copper, manganese, nickel, lead, and zinc; Group II, bismuth, tin, gallium, molybdenum, and gold; Group III, antimony, germanium, glucinum, titanium, tungsten, and vanadium. The elements of Group I have previously been detected in marine plants, those of Group II in sea-water, whilst those of Group III have not been previously reported as occurring either in sea-water or in marine plants. Gold, bismuth, germanium, and gallium were only present in spectrographic traces in the ashes examined.

W. G.

Application of the Biochemical Method to the Study of the Leaves of *Hakea laurina*. Extraction of a Glucoside (Arbutin) and of Quebrachitol. EM. BOURQUELOT and H. HÉRISSEY (*Compt. rend.*, 1919, **168**, 414—417).—From a study of the rotation of an extract of the leaves of *Hakea laurina*, R. Br., made by alcohol, after subsequent defecation and removal of the alcohol, first directly and then after the action, first, of invertase, and, secondly, of emulsin, the authors show the presence of sucrose, of two glucosides, and of a levorotatory substance, not hydrolysable by emulsin, in the leaves. By the use of suitable solvents they have isolated quebrachitol and arbutin in their crystalline forms and characterised them.

W. G.

Ovalbumin Constitutes a Complete Food for *Isaria densa*.

MARIN MOLLIARD (*Compt. rend.*, 1919, **168**, 523—524).—Ovalbumin, prepared from the commercial material by solution in water and subsequent coagulation by heat in such a manner as to obtain it as a very finely flocculated mass which is filtered off and strongly pressed, satisfies all the nutritive requirements of *Isaria densa*. The phenomena of intense oxidation of ovalbumin give rise to a very low respiratory quotient and the formation of oxalic acid.

W. G.

The Microchemical Reactions and Localisation of the Alkaloid of *Isopyrum thalictroides*, L. MARCEL MIRANDE (*Compt. rend.*, 1919, **168**, 316—317).—The author gives a number of microchemical tests for detecting the presence of the alkaloid, isopyrine, in the plant cells, and shows that it occurs, in the case of *Isopyrum thalictroides*, principally in the subterranean organs, which are at all seasons very rich in the alkaloid and to a less extent in the green aerial organs. [See, further, *J. Soc. Chem. Ind.*, 1919, 197A.]

W. G.

Organic Chemistry.

Graphic System of Representing Hydrocarbons. W. A. OSTWALD (*Chem. Zeit.*, 1919, **43**, 121—122).—If the percentage and relative proportional composition of hydrocarbons be graphically represented in a system in which the ratios of the percentages of hydrogen and carbon form the ordinates and the ratios of the number of atoms of hydrogen to carbon form the abscissæ, the connected points of intersection form a straight line terminated at one end by methane and at the other by pure carbon. On this line there are two well-marked points, that occupied by the olefines with the ratio of $H:C=2:1$ and the ratio of the percentages of $H:C=0.167$, and that occupied by benzene and acetylene with $H:C=1:1$ and $\%H:\%C=0.083$. The first point is approached by the paraffins, starting from methane, whilst the second point forms the starting place for the series of aromatic and acetylene hydrocarbons with increasing molecular weight (in the upward direction towards the olefine point), and also for the hydrocarbons rich in carbon and with many rings in their structure (in the downward direction leading towards pure carbon). By dropping as perpendiculars on to the line the molecular weights, a co-ordinated system is obtained in which, in the case of homologous series, the atoms of carbon as lines cut the atoms of hydrogen as curves. Analogous representations are obtained when the percentage of hydrogen and atoms of hydrogen, the percentage of carbon and atoms of carbon, the percentage of hydrogen and atoms of carbon, and the percentage of carbon and atoms of hydrogen are chosen as co-ordinates. For example, in a graphic representation on the last-named system, benzene, naphthalene, and anthracene lie on one curve, the continuation of which leads to chrysene, picene, and other hydrocarbons of multi-ringed structure. In the whole field, homologous series fall together in lines which show recognised chemical relationships.

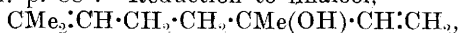
C. A. M.

Production of Ethyl Alcohol from Algæ. ED. KAYSER (*Ann. Chim. anal.*, 1919, [ii], **1**, 79—80).—The marine algæ *Laminaria flexicaulis* and *L. saccharina*, when heated with water under pressure, yield a liquid which ferments readily; about 3.7 litres of alcohol are obtained per 100 kilos. of dry algæ. If the digestion is made with 7% sulphuric acid and the liquid obtained nearly neutralised before fermentation, the yield of alcohol may be increased to about 12 litres. [See, further, *J. Soc. Chem. Ind.*, 1919, 266A.]

W. P. S.

Synthesis of Linalool. L. RUZICKA and V. FORNASIR (*Helv. Chim. Acta*, 1919, **2**, 182—188).—Tiemann and Semmler's formula for linalool has now been confirmed by synthesis. Methylhepten-

one (from citral; Verley, A., 1898, i, 557) is dissolved in ether, mixed with finely powdered sodamide, and then submitted to a slow current of acetylene at a low temperature, when a good yield of *dehydrolinalool*, $\text{CMe}_2\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}(\text{OH})\cdot\text{C}\equiv\text{CH}$, is obtained. This is a colourless, mobile oil, b. p. $91-93^\circ/12\text{ mm.}$, D^{15}_4 0.8855, with an odour like citral, and it forms a *phenyl-carbamate*, m. p. 88° . Reduction to linalool,



is effected by shaking an ethereal solution of the oil with thin shavings of sodium (8 atomic proportions) applied in four separate portions, a few drops of water being added from time to time.

J. C. W.

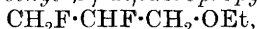
Spontaneous Inflammation of Mixtures of Air and Ethyl Ether Vapour. E. ALILAIRE (*Compt. rend.*, 1919, 168, 729—730).

—Under the experimental conditions, it was found that spontaneous inflammation of a mixture of air and ethyl ether vapour occurred at about 190° , when the amount of ether in the gaseous mixture was 1 gram per litre. No reaction took place at the ordinary temperature.

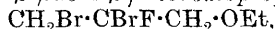
W. G.

Ethyl Fluorobromopropyl Ether and Ethyl Fluoroallyl Ether. FRÉD. SWARTS (*Bull. Soc. chim.*, 1919, [iv], 25, 103—107).

—Ethyl allyl ether when brominated yields *ethyl dibromopropyl ether*, $\text{CH}_2\text{Br}\cdot\text{CHBr}\cdot\text{CH}_2\cdot\text{OEt}$, b. p. $103.5^\circ/35\text{ mm.}$, which when heated with mercurous fluoride or silver fluoride gives ethyl bromide and a certain amount of *ethyl β -fluoro- γ -bromopropyl ether*, $\text{CH}_2\text{Br}\cdot\text{CHF}\cdot\text{CH}_2\cdot\text{OEt}$, b. p. $156.4-157.3^\circ$, D^{16}_4 1.484, together with a little *ethyl $\beta\gamma$ -difluoropropyl ether*



b. p. 114.5° . When heated with sodium methoxide in methyl-alcoholic solution, ethyl fluorobromopropyl ether yields *ethyl β -fluoroallyl ether*, $\text{CH}_2\text{CF}\cdot\text{CH}_2\cdot\text{OEt}$, b. p. 77.5° , $D^{15.1}_4$ 0.91659, n_D 1.37665, n_D 1.3790, n_D 1.38874, which readily combines with bromine, giving *ethyl β -fluoro- $\beta\gamma$ -dibromopropyl ether*,



b. p. 188° .

W. G.

Action of Alkyl Iodides on Normal Sodium Phosphate in Aqueous Solution. OCTAVE BAILLY (*Compt. rend.*, 1919, 168, 560—563).

—The lower members of the series of alkyl iodides react with normal sodium phosphate in aqueous solution when heated in sealed tubes at 60° or 100° , giving the disodium alkyl phosphates and a small amount of the monosodium dialkyl phosphates. The yield diminishes rapidly from 73.5% in the case of methyl iodide to 10.6% in the case of *isobutyl iodide* as the molecular weight increases. The following normal alkali and alkali-earth salts of the alkyl phosphates have been prepared: *strontium, potassium, ammonium*, and *sodium methyl phosphates*; *strontium and sodium ethyl phosphates*; *calcium and strontium propyl phosphates*;

calcium, strontium, and sodium isopropyl phosphates; calcium and strontium isobutyl phosphates; strontium allyl phosphate. The solubility of the alkali-earth alkyl phosphates diminishes from the barium salts through the strontium salts to the calcium salts, which are almost insoluble.

W. G.

Formic Acid is as much an Aldehyde. MAURICE PRUD'HOMME (*J. Chim. Phys.*, 1918, **16**, 438—441).—From a study of the heats of formation and combustion of formic acid, the author concludes that, under the conditions of temperature and pressure prevailing when combustion occurs, formic acid behaves as a mixture of equal parts of the tautomeric acid and hydroxy-aldehyde forms.

W. G.

Nature of the Fatty Acids produced by the Oxidation of Brown Coal Tar Oil. C. HARRIES (*Ber.*, 1919, **52**, [B], 65—72).—The fatty acids produced by treating brown coal-tar oil (freed from solid paraffins and phenols, and then having b. p. 125—220°/10 mm.) with ozone and decomposing the resulting ozonides (Harries, Koetschau, and Fonrobert, *Chem. Zeit.*, 1917, **16**, 117) have been esterified by Fischer's method, and the esters separated by fractional distillation. Formic, acetic, propionic, oxalic, palmitic, stearic, and myristic acids have been identified, and two other acids, probably heptonic and octonic acids, isolated. The complete absence of the fatty acids $C_4H_8O_2$ — $C_6H_{12}O_2$ is remarkable.

C. S.

Preparation of certain Organic Salts of Tellurium. AARON M. HAGEMAN (*J. Amer. Chem. Soc.*, 1919, **41**, 342—346).—*Tellurium hydrogen tartrate* is formed by heating at 70° tellurium dioxide with a solution of tartaric acid for several months. The solution may not be boiled, for a quantity of tellurium is thereby separated. Since the tartrate cannot be separated from tartaric acid by crystallisation, it is necessary to use the exact quantities required in the preparation. The pure salt has the formula $Te(HC_4H_4O_6)_4$. *Tellurium hydrogen citrate*, $Te(HC_6H_5O_7)_2$, is formed as a white, opaque, crystalline compound which separates in radiating clusters. It is produced by boiling tellurium dioxide with an aqueous solution of citric acid for a month. This compound does not deposit tellurium on boiling, and may be separated from citric acid by crystallisation. Succinic acid does not attack tellurium dioxide. Solutions of oxalic, lactic, malic, and gallic acids hold appreciable quantities of tellurium dioxide in solution, but it was found impossible to separate a crystalline compound of tellurium with any of these acids from solution. It is possible that an oleate and stearate of tellurium exist, but a pure, crystalline compound could not be obtained by the action of tellurium tetrachloride in benzene on a benzene solution of copper oleate or stearate.

J. F. S.

Polymerisation of Formaldehyde by Alkalies. C. MANNICH (*Ber.*, 1919, **52**, [B], 160—162).—By keeping 30% formaldehyde solution (almost free from methyl alcohol) containing 1—4% of anhydrous sodium carbonate, 0.3% of sodium hydroxide or 0.3% of calcium oxide for four months, crystals, the separation of which begins within one day, are obtained, which prove to be α -polyoxymethylene (Auerbach and Barschall, A., 1908, i, 131). The yield, which is 43% of the theoretical in the best case (with 4% of sodium carbonate), is diminished if methyl or ethyl alcohol is present. C. S.

Improvements in the Manufacture of Diethyl and Dimethyl Ketones. NEVIL VINCENT SIDGWICK and BERTRAM LAMBERT (*Brit. Pat.*, 14085 of 1915).—A practically quantitative yield of acetone or of diethyl ketone may be obtained by passing the vapour of acetic or propionic acid over manganous oxide at 350°. The process may be carried out either with or without the dilution of the acid with water, and an acid diluted to 20% may be used. The catalyst is prepared by boiling pumice stone in a strong aqueous solution or suspension of manganous acetate or carbonate, and continuing the boiling until all the water is evaporated, the temperature not being allowed to rise above 200° unless air is excluded. W. G.

Action of Neutral Salts on the Inversion of Sucrose by Acids. H. COLIN and M. LEBERT (*Bull. Assoc. Chim. Sucr. Dist.*, 1918, **35**, 14—17).—A study of the inhibitive influence of sodium acetate, sodium citrate, and potassium oxalate on the hydrolytic action of the respective acids and on that of hydrochloric acid. The results are in accord with the known retrogression of the degree of electrolytic dissociation of weak acids in presence of their salts. [See *J. Soc. Chem. Ind.*, 1919, May.] J. H. L.

Transformations of Nitrocellulose. A. ANGELI (*Atti R. Accad. Lincei*, 1919, [v], **28**, i, 20—24).—Nitrocellulose in the form of collodion cotton or guncotton is readily gelatinised by pyridine (compare Walter, A., 1911, i, 124), a large proportion of the latter yielding dense liquids which have the appearance of collodion, and gradually diminish in viscosity until, after a few days at the ordinary temperature, they resemble in this respect the pure pyridine; this phenomenon serves to detect unaltered cellulose in nitrocellulose. Treatment of the collodion cotton with just sufficient pyridine to moisten it yields a semi-solid, transparent mass with the appearance of caoutchouc, this also becoming continually more fluid until it is able to pass through filter paper. The yellow liquid thus formed smells strongly of pyridine, and with water gives an almost white mass, which has a resinous appearance and tenaciously retains pyridine. When freed from the latter by means of alcohol and dilute sulphuric acid, reprecipitated, washed, and dried over sulphuric acid, the product forms a white, amorphous powder, soluble readily in acetone and to a less extent

in alcohol, and almost insoluble in ether or benzene; the yield is about 80% of the collodion cotton used. The compound contains 9—10% of nitrogen, and somewhat resembles the substance obtained in small proportion by Berl and Fodor (A., 1911, i, 264) by treatment of very dilute alcoholic or ethereal solution of nitrocellulose with alkali hydroxide or sodium carbonate. It begins to turn brown at about 165°, and becomes almost black at 250°. When its alcoholic solution is poured into water, it forms a very stable, opalescent, colloidal solution, which is coagulated immediately by sodium chloride, ammonium sulphate, or gelatin solution, but is not precipitated by aqueous tannin solution. With benzene and sulphuric acid, it gives nitrobenzene, and with sulphuric acid in presence of mercury, nitric oxide. On a wet dimethylaminoazobenzene paper, it forms slowly an intensely red spot. It reduces ammoniacal silver nitrate and reacts readily with phenylhydrazine, but has no action on Fehling's solution. Quinoline and nicotine also act, but more slowly, on nitrocellulose.

T. H. P.

Origin of Creatine. III. KARL THOMAS and M. G. H. GOERNE (*Zeitsch. physiol. Chem.*, 1919, **104**, 73—87. Compare A., 1914, i, 353, 1110).—No increase in the urinary creatine was observed to follow the oral or subcutaneous administration of ϵ -methylguanidinohexoic acid or γ -methylguanidinobutyric acid to rabbits. The preparation of these acids and certain closely related compounds is described. *Toluenesulphonyl- ϵ -amino-*n*-hexoic acid*, $C_6H_4Me \cdot SO_2 \cdot NH \cdot [CH_2]_5 \cdot CO_2H$, crystallises from water in slender needles, m. p. 104—106°. *Toluenesulphonyl- ϵ -methylamino-*n*-hexoic acid*, $C_6H_4Me \cdot SO_2 \cdot NMe \cdot [CH_2]_5 \cdot CO_2H$, crystallises from water or ethyl acetate in white, slender needles, m. p. 55—59°. *ϵ -Methylamino-*n*-hexoic acid*, $NHMe \cdot [CH_2]_5 \cdot CO_2H$, crystallises with $1\frac{1}{2}$ molecules of water. The hydrated form melts indefinitely at 67°; the anhydrous form, crystallised from alcohol, melts at 132°.

ϵ -Methylguanidinohexoic acid, $NH_2 \cdot C(NH) \cdot NMe \cdot [CH_2]_5 \cdot CO_2H$, prepared from ϵ -methylamino-*n*-hexoic acid (ϵ -methyl-leucine) and cyanamide, crystallises with difficulty from water in microscopic tufts of needles. It decomposes without melting about 285°. The *hydrochloride* of this acid crystallises from alcohol in slender needles, m. p. 105°, and the *nitrate* melts indefinitely at 80—85°. For purposes of identification, the *acid orotate* serves best. This salt crystallises from water in needles, m. p. 167—168° (uncorr.). *ϵ -Methylcarbamido-*n*-hexoic acid*, $NH_2 \cdot CO \cdot NMe \cdot [CH_2]_5 \cdot CO_2H$, crystallises from water in stout needles, m. p. 163° (decomp.). *Toluenesulphonyl- γ -aminobutyric acid*,

$C_6H_4Me \cdot SO_2 \cdot NH \cdot [CH_2]_3 \cdot CO_2H$,
m. p. 135°, crystallises from water. *Toluenesulphonyl- γ -methylaminobutyric acid*, $C_6H_4Me \cdot SO_2 \cdot NMe \cdot [CH_2]_3 \cdot CO_2H$, m. p. 96—98°, crystallises from dilute alcohol. γ -Methylaminobutyric acid is very hygroscopic. *γ -Methylguanidinobutyric acid*,
 $NH_2 \cdot C(NH) \cdot NMe \cdot [CH_2]_3 \cdot CO_2H$,

was not obtained in the pure condition. γ -Carbamidobutyric acid, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot[\text{CH}_2]_3\cdot\text{CO}_2\text{H}$, m. p. $175\text{--}176^\circ$ (decomp.), crystallises from water or alcohol.

J. C. D.

Bromination of Unsaturated Compounds with *N*-Bromoacetamide. The Law of the Course of Chemical Reactions.

A. WOHL (*Ber.*, 1919, **52**, [B], 51—63).—In the presence of cold acetone or ethyl ether as solvent, acetobromoamide reacts with certain substances as a brominating agent, acetamide being produced, but not hydrogen bromide. Thus *tert.*-butyl bromide is converted into *isobutylene* dibromide, phenol into *p*-bromophenol, anisole into *p*-bromoanisole, ethyl acetoacetate into ethyl α -bromoacetoacetate, and the half-amide of malonic ester into the half-amide of bromomalonic ester. $\beta\gamma$ -Dimethyl- Δ^β -butene yields α -bromo- $\beta\gamma$ -dimethyl- Δ^β -butene amongst other products. β -Methyl- Δ^β -butene in ethereal solution yields dibrominated and more highly brominated products, but in acetone solution with 2 mols. of acetobromoamide it yields an unsaturated dibromo-derivative. In acetone solution, γ -bromo- β -methyl- Δ^β -butene can be further brominated by acetobromoamide, and yields an unsaturated dibrominated product.

In the reactions between acetobromoamide and the preceding unsaturated compounds, there is no addition of fragments of the acetobromoamide molecule at the double linking, but the whole molecule must become attached to one of the carbon atoms by residual affinity; an interchange of hydrogen and bromine occurs between the two molecules, and acetamide and a bromine-substituted derivative of the unsaturated compound are produced.

C. S.

Mercury Fulminate and some of its Impurities. PAUL NICOLARDOT and JEAN BOUDET (*Bull. Soc. chim.*, 1919, [iv], **25**, 119—122).—Sodium and ammonium thiosulphates in 5% aqueous solutions are much more satisfactory solvents than potassium cyanide at the same concentration for analytical purposes, since they do not dissolve the impurities likely to be present in the fulminate, whilst these are soluble in the potassium cyanide solution. Heaven's method (*A.*, 1918, ii, 233) for the estimation of mercury fulminate may be applied to the extract made with either of the thiosulphates. For the method of recovery of mercury from the residues in the manufacture of mercury fulminate, see *J. Soc. Chem. Ind.*, 1919, May.

W. G.

Organic Fluorine Compounds. III. I. J. RINKES (*Chem. Weekblad*, 1919, **16**, 206—213).—The assertion of Meyer and Hub (*A.*, 1910, i, 735) that by means of the Hoffmann reaction no fluoroaniline is obtained from *o*-fluorobenzamide is disproved, the reaction being, on the contrary, an excellent preparative method giving good yields of fluoroaniline. *o*-Fluorobenzamide was prepared from *o*-toluidine by diazotising in presence of hydrofluoric

acid. The oxidation of the *o*-fluorotoluene is effected by the chlorination of the methyl group and subsequent hydrolysis, which permits of the preparation of the aldehyde. This method is preferable to the direct oxidation by means of permanganate. *p*-Fluorobenzaldehyde was prepared in a similar way, and with hydroxylamine hydrochloride and sodium carbonate gives directly *p*-fluoroantialdoxime (m. p. 81.2°). Regeneration of the oxime from the hydrochloride by means of sodium carbonate gives *p*-fluorosynaldoxime (m. p. $116-117^{\circ}$). *o*-Fluorobenzaldoxime hydrochloride on treatment with sodium carbonate yields the original antialdoxime. This behaviour is analogous to that of *o*- and *p*-chlorobenzaldoximes.

o-Fluoriodobenzene, b. p. $188.6^{\circ}/759$ mm., was prepared from *o*-fluoroaniline by diazotising and adding potassium iodide.

p-Fluoriodobenzene, b. p. $183.2^{\circ}/760$ mm., was prepared in a similar way. This was obtained in two crystalline forms, m. p. -27.2° and -18° respectively.

An attempt to prepare fluorine derivatives of iodobenzene with fluorine in the nucleus was unsuccessful. Phenyl iododifluoride was first prepared from iodosobenzene and fuming hydrofluoric acid. This was kept for three months in a copper tube. No formation of fluoroiodobenzene was observed, the principal product being apparently diphenyl.

p-Fluoronitrosobenzene was prepared from *p*-fluoroaniline by oxidation by means of ammonium persulphate, and its behaviour studied with respect to condensation in concentrated sulphuric acid. The chief condensation product was found to be 2:7-difluorophenazine-5:10-oxide, brownish-yellow needles, m. p. 150° , analogous to the corresponding chlorine derivative obtained by Bamberger and Ham (A., 1911, i, 684).

W. S. M.

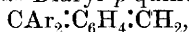
Catalytic Dehydrogenation by Nickel in the Presence of Hydrogen. PAUL SABATIER and GEORGES GAUDION (*Compt. rend.*, 1919, **168**, 670—672).—Hydrocarbons of the benzene series when passed with hydrogen over nickel at 180° undergo hydrogenation, but if the temperature is raised to $350-360^{\circ}$, dehydrogenation occurs. Thus at this higher temperature pinene yields a mixture of cymene and cumene; limonene and camphene yield the same mixture; menthene gives cymene; cyclohexene gives benzene; cyclohexanol gives phenol; pulegone gives a mixture of cresol and thymol; eucalyptol, terpene, and terpineol undergo dehydration as well as dehydrogenation. The presence of hydrogen is essential for this dehydrogenation.

W. G.

Formation and Stability of spiro-Compounds. II. Bridged-spiro-compounds Derived from cyclo-Hexane. CHRISTOPHER KELK INGOLD and JOCELYN FIELD THORPE (T., 1919, **115**, 320—383).

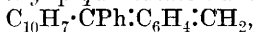
Solubilities, Separation, and Purification of Anthracene, Carbazole, and Phenanthrene. JOHN MARSHALL CLARK (*J. Ind. Eng. Chem.*, 1919, **11**, 204—209).—Various solvents have been proposed for separating anthracene, carbazole, and phenanthrene from the "anthracene oil" of coal tar, but none effects complete separation, and chemical methods are required to complete the purification. At 15.5°, benzene dissolves 1.04% of anthracene, 0.72% of carbazole, and 16.72% of phenanthrene; acetone dissolves 0.55% of anthracene, 6.12% of carbazole, and 15.08% of phenanthrene; and light pyridine, 0.85%, 12.45%, and 25.54% of the respective substances. In the method described, crude coal-tar solvent naphtha is used to remove the phenanthrene, and pyridine to separate carbazole from anthracene. The anthracene is then purified by fusion with alkali, to retain the carbazole and sublimation, whilst carbazole is purified by treatment with 98% sulphuric acid, which combines with anthracene to form a sulphonated compound soluble in a large volume of water, whilst the carbazole is scarcely affected. In the fusion with alkali, the best results are obtained by the use of a mixture of potassium and sodium hydroxides. [See, further, *J. Soc. Chem. Ind.*, 1919, 247A.] C. A. M

***p*-Quinodimethanes.** W. SCHLENK and EGON MEYER (*Ber.*, 1919, **52**, [B], 8—21).—*as*-Diaryl-*p*-quinodimethanes,



have now been prepared, essentially by Tschitschibabin's method (A., 1908, i, 872), but in some cases the product is difficult (or impossible) to isolate on account of its tendency to polymerise. Thus, *as*-diphenyl-, *as*-phenyl-*p*-tolyl-, and *as*-phenyldiphenylquinodimethanes could not be isolated, and *as*-di- α -naphthylquinodimethane could only be obtained in solution.

By keeping at the ordinary temperature, or more rapidly by warming, a solution of phenyl-*p*-tolyl- α -naphthylchloromethane in pyridine with the complete exclusion of air and in the absence of light, *as*-phenyl- α -naphthyl-*p*-quinodimethane,



is obtained. Its isolation is difficult but the substance is ultimately obtained as a dark blue powder. Its solutions are intensely bluish-violet, and in the dilute state exhibit a green fluorescence. Its ethereal solution is instantly decolorised by oxygen, chlorine, bromine, or ferric chloride. The tendency to polymerise is relatively small, but it does polymerise, frequently without obvious cause.

In a similar manner, phenyl-*o*-tolyl-*p*-tolylchloromethane yields *as*-phenyl-*o*-tolyl-*p*-quinodimethane, $\text{C}_7\text{H}_7\cdot\text{CPh}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2$, violet powder, which is somewhat more stable than the preceding compound towards oxygen.

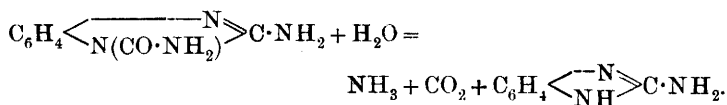
The intense colour of these two diarylquinodimethanes in comparison with that of tetra-arylquinodimethanes is very remarkable; also in solution they exhibit selective absorption in the visible

spectrum, whereas the tetra-aryl compounds show continuous absorption.

Phenyl-p-tolyl-α-naphthylcarbinol, $C_{10}H_7 \cdot CPh(C_7H_7) \cdot OH$, prepared in the usual way from magnesium α-naphthyl bromide and phenyl *p*-tolyl ketone, is a colourless, crystalline powder, m. p. 109—110°, which is converted by hydrogen chloride in ethereal solution into *phenyl-p-tolyl-α-naphthylchloromethane*, m. p. 142—144°. *Phenyl-o-tolyl-p-tolylchloromethane*, prepared in a similar manner, has m. p. 86·5°. *Phenyl-o-tolyl-diphenylcarbinol*, colourless crystals, m. p. 137—138°, and the *chloride*, $C_6H_4Ph \cdot CPhCl \cdot C_7H_7$, m. p. 161°, are described. *p-Tolyl-di-α-naphthylcarbinol* could not be isolated in a pure state, since by repeated crystallisation it is changed to *p-tolyl-di-α-naphthylfluorene*, $\begin{matrix} C_{10}H_6 \\ C_{10}H_6 \end{matrix} > C(OH) \cdot C_7H_7$, needles, m. p. 162·5—163°.

C. S.

***o*-Aminophenylcarbamide.** GUIDO PELLIZZARI (*Gazzetta*, 1919, 49, i, 16—26).—This compound, prepared by a method simpler than that used by Schiff and Ostrogovich (A., 1897, i, 144) for its meta- and para-isomerides, has basic properties, and treatment of its hydrochloride with potassium cyanate yields *o*-phenylenedicarbamide. At 150°, it loses quantitatively 1 mol. of ammonia, giving *o*-phenylenecarbamide, which is prepared most simply in this way. Treatment of *o*-phenylenediamine with cyanogen bromide yields *o*-phenyleneguanidine, but in the case of *o*-aminophenylcarbamide, this reagent gives first *o*-cyanoaminophenylcarbamide, which is an acid compound stable in dry air, but is gradually changed by moist air or by water into the metameric basic compound, *o*-phenylene-α-guanylcabamide. The latter cannot be obtained pure in the free state, since it is hygroscopic and tends to undergo hydrolysis into *o*-phenyleneguanidine, ammonia, and carbon dioxide:



This decomposition, which occurs slowly in the cold and more rapidly in the hot, is greatly accelerated by the presence of either alkali or mineral acid. Thus the salts of *o*-phenylene-α-guanylcabamide could not, in general, be prepared, although the action of picric acid on cold aqueous *o*-cyanoaminophenylcarbamide yields the picrate, which is decomposed similarly by hot water, *o*-phenyleneguanidine picrate crystallising out from the solution.

The existence of this highly unstable *o*-phenylene-α-guanylcabamide confirms the constitutional formulæ attributed to the two cyano-derivatives described previously (this vol., i, 134).

o-Aminophenylcarbamide, $NH_2 \cdot C_6H_4 \cdot NH \cdot CO \cdot NH_2$, prepared by the action of potassium cyanate (1 mol.) on *o*-phenylenediamine

k*

monohydrochloride (1 mol.), forms shining needles, and shows signs of melting at 175° , then becomes opaque, and melts at 307° ; in a moist atmosphere, it has m. p. 175° (decomp.), a solid residue, m. p. 307° , which is that of *o*-phenylenecarbamide, remaining. Its *picrate*, $C_7H_9ON_3 \cdot C_6H_3O_7N_3$, forms an almost gelatinous, felted mass of long, very slender needles, decomposing at 200 — 235° . The *nitrate*, $C_7H_9ON_3 \cdot HNO_3 \cdot \frac{1}{2}H_2O$, long, white needles, reddens at 170 — 175° , and then contracts and undergoes gradual alteration. The hydrochloride and platinichloride crystallise well and are moderately soluble.

o-Cyanoaminophenylcarbamide, $CN \cdot NH \cdot C_6H_4 \cdot NH \cdot CO \cdot NH_2$, forms small, white, shining crystals, and decomposes at 110° .

o-Phenylene- α -guanilycarbamide *picrate*, $C_8H_8ON_4 \cdot C_6H_3O_7N_3$, forms a yellow powder and decomposes at 250 — 260° . T. H. P.

Compounds of Phenols, Phenolic Ethers, and Salicylaldehyde with Normal Salts. R. F. WEINLAND and GUSTAV BÄRLOCHER (*Ber.*, 1919, **52**, [B], 147—159).—An extension of the work of Weinland and Denzel (*A.*, 1914, i, 953; 1915, i, 526). *Compounds* of the type $CaX_2 \cdot 4C_6H_4(OH)_2 \cdot 2R \cdot OH$ have been obtained, where X is Cl, Br or I, and R is Me, Et, Pr^a, or C_5H_{11} , from solutions of catechol and the calcium haloid (anhydrous) in the respective alcohols; they all form colourless crystals which are stable over sulphuric acid. Quinol forms similar compounds, but less readily, whilst resorcinol does not.

Quinol forms *compounds*, colourless crystals, with potassium formate, acetate, and propionate, $H \cdot CO_2K \cdot 2C_6H_4(OH)_2$,

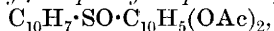
$2CH_3 \cdot CO_2K \cdot 3C_6H_4(OH)_2$, and $C_2H_5 \cdot CO_2K \cdot 2C_6H_4(OH)_2$. Pyrogallol forms *compounds*, $KA \cdot C_6H_3(OH)_3$, with the same three salts, whilst phloroglucinol forms the *compound* $CH_3 \cdot CO_2K \cdot C_6H_3(OH)_3$. All these compounds crystallise from alcoholic solutions of the components.

Compounds, colourless, stable crystals, have been obtained from guaiacol (2 mols.) and potassium formate, acetate, propionate or butyrate (1 mol.), guaiacol (2 mols.) and sodium acetate (1 mol.), eugenol (2 mols.) and potassium propionate (1 mol.), vanillin (1 mol.) and potassium propionate (1 mol.), vanillin (3 mols.) and potassium acetate, propionate or butyrate (2 mols.), and vanillin (2 mols.) and potassium formate or sodium acetate (1 mol.).

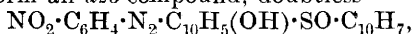
Compounds, pale yellow, stable needles, have been obtained from alcoholic solutions of salicylaldehyde (2 mols.) and potassium acetate, propionate or butyrate (1 mol.). C. S.

Derivatives of *iso*- α -Naphthyl-1:4-dihydroxy- β -naphthylsulphone. O. HINSBERG (*Ber.*, 1919, **52**, [B], 28—35).—An instance of stereoisomerism analogous to that of the β -naphthol sulphides is described. α -Naphthyl-1:4-dihydroxy- β -naphthylsulphone (*A.*, 1917, i, 575) undoubtedly belongs to the normal series of sulphones. By heating at 170° , it loses 1 mol. of water, and is converted into a *substance*, brownish-red, crystalline powder, sintering at 85° and

completely molten at 105° , which undoubtedly has the formula $C_{10}H_7 \cdot SO \cdot C_{10}H_5O_2$, and, on account of its ready solubility, low and indefinite m. p., and intense colour, belongs to the *iso*-series, and is therefore *iso- α -naphthyl-2- α -naphthaquinonylsulphoxide* (two by-products are formed in this reaction, the one a grey, very sparingly soluble substance, the other, yellow crystals, m. p. 225° [decomp.]). The *iso*-sulphoxide is reduced and acetylated by zinc dust and acetic anhydride on the water-bath, yielding *iso- α -naphthyl-1:4-diacetoxy- β -naphthylsulphoxide*,



pale yellow, crystalline powder containing $\frac{1}{2}CHCl_3$ (from chloroform), decomp. 73° and completely molten at 105° . The *iso*-sulphoxide combines with *p*-nitrophenylhydrazine in warm glacial acetic acid to form an *azo*-compound, doubtless

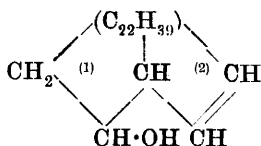


red powder, and is oxidised in warm glacial acetic acid solution by 30% hydrogen peroxide, yielding *iso- α -naphthyl-2- α -naphthaquinonylsulphone*, $C_{10}H_7 \cdot SO_2 \cdot C_{10}H_5O_2$, yellowish-brown needles or crusts containing $\frac{1}{2}H_2O$, m. p. $110-115^{\circ}$ (decomp.), which is quite different from the isomeric α -naphthyl-2- α -naphthaquinonylsulphone (*loc. cit.*), exhibits its quinone nature by reacting with aniline and with *p*-nitrophenylhydrazine, and is reduced and acetylated by zinc dust and acetic anhydride, yielding a colourless substance, probably *iso- α -naphthyl-1:4-diacetoxy- β -naphthylsulphone*.

C. S.

Cholesterol. XXVI. Ring Systems in Cholesterol. A.

WINDAUS and O. DALMER (*Ber.*, 1919, **52**, [B], 162—169).—Investigations demonstrative of the number of atoms in the two ring systems of the cholesterol molecule (Windaus, A., 1917, i, 265) have not hitherto been undertaken. The authors attack the problem as follows. By hydrogenation at the double linking



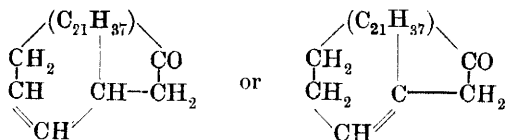
(annexed formula), ring 2 is rendered proof against oxidation, and ring 1 is then ruptured; if, on the other hand, the hydroxyl group in ring 1 is replaced by hydrogen, ring 2 is then ruptured on oxidation. In both cases, dicarboxylic acids are obtained, in which the positions

of the carboxyl groups are determined with great probability by Blanc's method with acetic anhydride (A., 1907, i, 710).

Dihydrocholesterol (β -cholestanol), obtained by reducing cholesterol in acetic acid solution at 100° with hydrogen and palladium, is oxidised to the dicarboxylic acid, $C_{27}H_{46}O_4$ (Windaus and Uibrig, A., 1914, i, 1066). By heating with acetic anhydride until the reagent has distilled completely, and then at $250^{\circ}/15-20$ mm., this acid is converted into a *ketone*, $C_{26}H_{44}O$, leaflets, m. p. $100-100.5^{\circ}$ (*oxime*, needles, m. p. 203°), which is oxidised by glacial acetic and nitric (D 1.48) acids at $75-80^{\circ}$ to a dibasic acid, $C_{26}H_{44}O_4$, needles, m. p. $234-235^{\circ}$. This acid, by treatment

with acetic anhydride and subsequent heating in a vacuum, yields its *anhydride*, $C_{26}H_{42}O_3$, crystals, m. p. 153° . The carboxyl groups in this acid, therefore, are in the 1:5-positions, those in the acid $C_{27}H_{46}O_4$ are in the 1:6-positions, and ring 1 of the cholesterol molecule contains six atoms of carbon.

Cholestene did not prove a suitable material for the rupture of ring 2, since it did not yield the desired dicarboxylic acid on oxidation. Therefore α -chlorocholestanone in alcoholic solution was converted by 20% potassium hydroxide at 50° into *heterocholestenone*,



needles, m. p. 96° , which was reduced in glacial acetic acid solution by hydrogen and palladium to *heterocholestanone*, $C_{27}H_{46}O$, leaflets, m. p. $98-99^\circ$ (*oxime*, needles, m. p. 195°). The latter ketone, which can also be obtained by reducing nitrocholestene with zinc dust and acetic acid, and yields cholestane by reduction by Clemmensen's method, is converted by glacial acetic and nitric (D 1.48) acids at $70-75^\circ$ into a dibasic acid, $C_{27}H_{46}O_4$, needles, m. p. 273° (decomp.), which yields its *anhydride*, $C_{27}H_{44}O_3$, needles, m. p. 118° , by treatment with acetic anhydride and subsequent distillation in a vacuum. The carboxyl groups in the acid $C_{27}H_{46}O_4$, therefore, are in the 1:4- or 1:5-positions. Only the latter alternative is permissible, and ring 2 therefore contains five atoms of carbon. On the assumption, therefore, that Blanc's method gives trustworthy results in the case of complicated cyclic structures, the constitution of the cholesterol molecule has been elucidated to the extent indicated in the annexed formula.

C. S.

Cholesterol. XXVII. Isomerism of Cholestane and ψ -Cholestane. A. WINDAUS (*Ber.*, 1919, 52, [B], 170—176. Compare preceding abstract).—Cholestane is without doubt the normal dihydro-derivative of cholestene. ψ -Cholestene, which yields ψ -cholestane by reduction in ethereal solution by hydrogen and platinum (Mauthner, A., 1907, i, 921; 1909, i, 714), is now found to give cholestane almost exclusively when reduced in glacial acetic acid solution by hydrogen and palladium at 75° . Cholestene and ψ -cholestene, therefore, differ only in the position of the double linking. ψ -Cholestane can therefore very well be a diastereoisomeride of cholestane, ring 2 (*loc. cit.*) being affixed to ring 1 in the *cis*-position. Some experimental observations support the new formulation. Dihydrocholesterol, derived from cholestane, is con-

verted through the acid $C_{27}H_{46}O_4$ into the ketone $C_{26}H_{44}O$ (*loc. cit.*). Coprosterol, derived from ψ -cholestane, yields by oxidation the isomeric acid $C_{27}H_{46}O_4$, which by evaporation with acetic anhydride and subsequent distillation in a vacuum is converted into an isomeric *ketone*, $C_{26}H_{44}O$, needles, m. p. 73—74°. The very smooth course of the ketone formation indicates that the two carboxyl groups in the two isomeric acids are in the *cis*-position. The acid $C_{27}H_{44}O_4$ obtained from cholesterol by Diels and Abderhalden (A., 1904, i, 880) is reduced in glacial acetic acid solution at 100° by hydrogen and palladium to a third isomeric acid, $C_{27}H_{46}O_4$, leaflets, m. p. 252° (*methyl ester*, $C_{29}H_{50}O_4$, prisms, m. p. 123—124°), which is converted by the acetic anhydride method, although far less smoothly, into the ketone, $C_{26}H_{44}O$, obtained from coprosterol through the second isomeric acid $C_{27}H_{46}O_4$. It is extremely probable, therefore, that the two acids $C_{27}H_{46}O_4$ last mentioned only differ from one another in that the two carboxyl groups in the former (which is less readily converted into the ketone) are in the *trans*-position, and in the latter are in the *cis*-position.

C. S.

Molecular Transpositions of α -Glycols. II. Product of Dehydration of $\alpha\beta\gamma$ -Triphenylpropan- $\alpha\beta$ -diol. A. ORÉKHOFF

(*Bull. Soc. chim.*, 1919, [iv], **25**, 108—111. Compare this vol., i, 146).—Magnesium benzyl chloride condenses with benzoin to give $\alpha\beta\gamma$ -triphenylpropan- $\alpha\beta$ -diol, $CH_2Ph \cdot CPh(OH) \cdot CHPh(OH)$, m. p. 159—160°, giving a *monoacetyl* derivative, m. p. 176—177°. The glycol, when dehydrated with sulphuric acid, yields *benzyl diphenylmethyl ketone*, $CHPh_2 \cdot CO \cdot CH_2Ph$, m. p. 80—81°, giving an *oxime*, m. p. 134—135°, and a *phenylhydrazone*, m. p. 99—100°. This ketone, when heated with alcoholic potassium hydroxide, is decomposed, giving diphenylmethane and potassium phenylacetate, and when condensed with magnesium benzyl chloride yields $\beta\beta$ -diphenyl- $\alpha\alpha$ -dibenzylethyl alcohol, $CHPh_2 \cdot C(C_6H_5)_2 \cdot OH$, m. p. 92—93°, which is also obtained by condensing ethyl diphenylacetate with magnesium benzyl chloride.

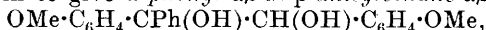
W. G.

Molecular Transpositions of α -Glycols. III. The Dehydration of $\alpha\gamma$ -Diphenyl- β -benzylpropan- $\alpha\beta$ -diol. A. ORÉKHOFF

(*Bull. Soc. chim.*, 1919, [iv], **25**, 111—115. Compare preceding abstract).—[With J. ZIVE].—Magnesium benzyl chloride condenses with methyl phenylglycollate to give $\alpha\gamma$ -diphenyl- β -benzylpropan- $\alpha\beta$ -diol, $CHPh(OH) \cdot C(CH_2Ph)_2 \cdot OH$, m. p. 110—111°, giving a *monoacetyl* derivative, m. p. 125—126°. The glycol, when dehydrated with sulphuric acid, yields *benzyl $\alpha\beta$ -diphenylethyl ketone*, $CH_2Ph \cdot CHPh \cdot CO \cdot CH_2Ph$, m. p. 75—76°, giving an *oxime*, m. p. 77—78°, and a *phenylhydrazone*, m. p. 126—127°. This ketone condenses with magnesium benzyl chloride to give $\alpha\beta\delta$ -triphenyl- γ -benzylbutan- γ -ol, $CH_2Ph \cdot CHPh \cdot C(CH_2Ph)_2 \cdot OH$, m. p. 122—123°, identical with the product obtained by the action of magnesium benzyl bromide on methyl $\alpha\beta$ -diphenylpropionate.

W. G.

Molecular Transpositions of the α -Glycols. IV. Product of Dehydration of a Methoxy-derivative of $\alpha\beta\beta$ -Triphenylethanedial. Phenylic Migration. A. ORÉKHOFF (*Bull. Soc. chim.*, 1919, [iv], 25, 115—118. Compare preceding abstract).—[With F. COMA-Y-ROCA.]—Magnesium phenyl bromide condenses with *p*-anisoin to give α -phenyl- $\alpha\beta$ -di-*p*-anisylethane- $\alpha\beta$ -diol,



m. p. 163—164°, which when dehydrated with sulphuric acid yields phenyl-di-*p*-anisylacetaldehyde, $\text{CHO}\cdot\text{CPh}(\text{C}_6\text{H}_4\cdot\text{OMe})_2$, m. p. 88—89°, giving an *oxime*, m. p. 132—133°, and a *semicarbazone*, m. p. 186—187°. This aldehyde is decomposed by alcoholic potassium hydroxide, giving phenyl-di-*p*-anisylmethane, m. p. 100—101° (compare Feuerstein and Lipp, A., 1902, i, 768).

W. G.

β -Bromoethyl *p*-Nitrobenzoate. THE ABBOTT LABORATORIES, (Brit. Pat., 121578).—The β -bromoethyl ester of *p*-nitrobenzoic acid is prepared by heating a salt of *p*-nitrobenzoic acid with an excess of ethylene bromide, preferably in the presence of an amine or of finely divided copper as a catalyst. A mixture of 15 grams of the dry sodium salt, 75 grams of ethylene bromide, and 0.5—1.0 c.c. of diethylamine is heated in a sealed tube at 140° for five hours. The product is neutralised, the excess of ethylene bromide is removed by distillation with steam, and the residue of β -bromoethyl *p*-nitrobenzoate is separated from a small quantity (about 4 grams) of the di-*p*-nitrobenzoic ester of ethylene glycol, which is formed as a by-product, by means of a suitable solvent, such as ether. The yield of crude product is about 15 grams; the pure β -bromoethyl ester has m. p. 51—52°, and may be converted into novocaine (diethyl-aminoethyl *p*-aminobenzoate) by combination with diethylamine and reduction of the nitro-group.

J. F. B.

Application of Acetylated Phenolcarboxylic Acids to the Synthesis of Depsides. EMIL FISCHER and A. REFIK KADISADÉ (*Ber.*, 1919, 52, [B], 72—77).—Acetylated phenolcarboxylic acids can be used instead of the methylcarbonato-derivatives for the synthesis of the simpler depsides, but the advantages of the new method over the old are not so marked as in the case of the synthesis of digallic acid (A., 1918, i, 172). 4-*p*-Acetoxybenzoyloxybenzoic acid, $\text{OAc}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, microscopic needles or long leaflets, m. p. 221—223° (corr.) with previous sintering, is precipitated in the form of its sodium salt when an ethereal solution of *p*-acetoxybenzoyl chloride and aqueous sodium hydroxide are added gradually, with cooling, to a solution of *p*-hydroxybenzoic acid in aqueous sodium hydroxide (1 mol.). In a similar way, 4-*p*-hydroxybenzoyloxybenzoic acid is converted into the acetylated tridepside, and *p*-hydroxybenzoic acid and triacetyl-galloyl (triacetoxybenzoyl) chloride yield *p*-triacetoxybenzoyloxy-

benzoic acid, $\text{C}_6\text{H}_5(\text{OAc})_3 \cdot \text{CO} \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, microscopic leaflets, m. p. 172—173° (corr.). C. S.

The Products of the Addition of Benzilic Acid to Aryl Thiocarbimides. H. BECKER and A. BISTRZYCKI (*Helv. Chim. Acta*, 1919, **2**, 111—117).—In an earlier paper (A., 1915, i, 245), it was shown that benzilic acid and phenylthiocarbimide react to form *N*-phenyl-*S*-benzhydrylthiocarbamate- α -carboxylic acid. The three *N*-tolyl derivatives, $\text{C}_6\text{H}_4\text{Me} \cdot \text{NH} \cdot \text{CO} \cdot \text{S} \cdot \text{CPh}_2 \cdot \text{CO}_2\text{H}$, have now been obtained from the tolylthiocarbimides in the same way, the yields being excellent; the *ortho*-derivative forms colourless tablets, decomp. 139°, the *meta*-compound decomposes at 141°, and the *para*- at 138.5°.

These acids readily lose carbon dioxide when heated at 60—100° with pyridine, the products being the *S*-benzhydryl *N*-arylthiocarbamates, $\text{NHAr} \cdot \text{CO} \cdot \text{S} \cdot \text{CHPh}_2$. The *phenyl* derivative forms bundles of needles, m. p. 135—136°; the *o*-tolyl compound crystallises in long needles, m. p. 123.5—124.5°; the *m*-tolyl compound forms glistening leaflets, m. p. 101—102.5°; and the *p*-tolyl derivative forms long prisms, m. p. 149.5—151°.

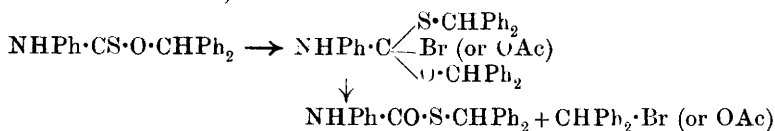
When the acids are boiled with methyl alcohol and concentrated sulphuric acid, they yield internal anhydrides, namely, the 5 : 5-diphenyl-3-arylthiazolid-2 : 4-diones, $\text{S} \begin{smallmatrix} \text{CO} \cdots \text{NAr} \\ \diagup \quad \diagdown \\ \text{CPh}_2 \quad \text{CO} \end{smallmatrix}$, as

follows: the 3-phenyl derivative, long, glistening prisms, m. p. 147.5—148.5°; the *o*-tolyl compound, large, granular masses of hexagonal prisms, m. p. 108—109°; the *m*-tolyl compound, rectangular prisms, m. p. 96.5—97.5°; the *p*-tolyl compound, flat needles, m. p. 105.5—106.5°.

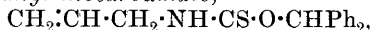
Benzilic and thiobenzilic acids react with undiluted phenylcarbimide at 100° to form *s*-diphenylcarbamide. It is reported that this substance suffers decomposition to a certain extent when melted (at about 234°) or distilled (about 260°). J. C. W.

Transformations of some *O*-Esters of Arylated or Alkylated Thiocarbamic Acids. A. BETTSCHART and A. BISTRZYCKI (*Helv. Chim. Acta*, 1919, **2**, 118—132).—In their first communication on the condensation of benzilic acid with arylthiocarbimides in the presence of pure acetic and sulphuric acids (A., 1915, i, 245), Becker and Bistrzycki offered an explanation of the mechanism of the unusual reaction, which has now been tested and found to be justified. They assumed that the first product was the expected *O*-ester, $\text{NHAr} \cdot \text{CS} \cdot \text{O} \cdot \text{CPh}_2 \cdot \text{CO}_2\text{H}$. Attempts to isolate such esters have failed, but closely related substances, with which the theory can be tested, have now been obtained by the action of the thiocarbimides on the sodium compound of benzhydryl dissolved in xylene. These esters may be transformed readily into the *S*-esters, $\text{NHAr} \cdot \text{CO} \cdot \text{S} \cdot \text{CHPh}_2$, by boiling with glacial acetic acid, although in the case of the phenyl compound many other methods have been found, including heating at

130—135°, or treatment with cold hydrochloric acid. The transformations by means of acids are explained by assuming that a little benzhydrol is liberated by hydrolysis, and is then attached at the $-C:S$ group in the form of its acetate or chloride, which is then eliminated again from the other position. Theoretically, therefore, a trace of such an ester should cause the transformation of an unlimited amount of *O*-ester into *S*-ester, and the whole theory is neatly proved by the fact that the change can indeed be brought about by heating with a small quantity of benzhydryl acetate or bromide in toluene, thus:



The following *O*-benzhydryl *N*-arylthiocarbamates are described; their isomerides have been made in the above manner, but are also mentioned in the previous abstract: The *phenyl* derivative, quadratic prisms, m. p. 123—123.5°; the *o*-tolyl compound, m. p. 123.5—124° (decomp.); and the *p*-tolyl compound, decomp. 126.5°. *O*-Benzhydryl *N*-allylthiocarbamate,

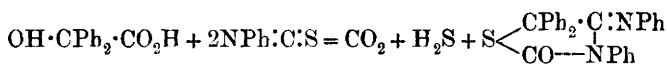


has also been prepared, in quadratic prisms, m. p. 59.5—61.5°, and converted into the *isomeride*, $\text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CO} \cdot \text{S} \cdot \text{CHPh}_2$, which forms very long prisms, m. p. 114.5—116.5°.

This transformation seems to depend on the nature of the group which wanders, for the benzyl derivative, $\text{NPh} \cdot \text{CS} \cdot \text{O} \cdot \text{CH}_2\text{Ph}$, is not so changed by acetic acid.

Benzilic acid will not condense with alkylthiocarbimides under the conditions employed in the earlier cases, but if phosphoric oxide is added as well as sulphuric acid, the same kind of reaction takes place. Ordinary mustard oil gives *N*-allyl-*S*-benzhydrylthiocarbamate- α -carboxylic acid, $\text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CO} \cdot \text{S} \cdot \text{CPh}_2 \cdot \text{CO}_2\text{H}$, prisms, decomp. about 133°, which is quantitatively converted into α -thioldiphenylacetic acid by boiling with 1% potassium hydroxide (a more convenient preparation than the earlier one, *loc. cit.*), or may be changed into the above *S*-benzhydryl *N*-allylthiocarbamate by heating with pyridine. *N*-isoButyl-*S*-benzhydrylthiocarbamate- α -carboxylic acid, rhombic tablets, m. p. 123—124° (decomp.), and *S*-benzhydryl *N*-isobutylthiocarbamate, long, silky prisms, m. p. 73.5—75°, have also been obtained.

In the hope of getting a normal *O*-ester from benzilic acid and phenylthiocarbimide, these substances have been heated together without diluents at 100°. A reaction, represented by the equation



was found to take place, the product being 4-phenylimino-3:5:5-triphenylthiazolid-2-one, which crystallises in prisms, m. p.

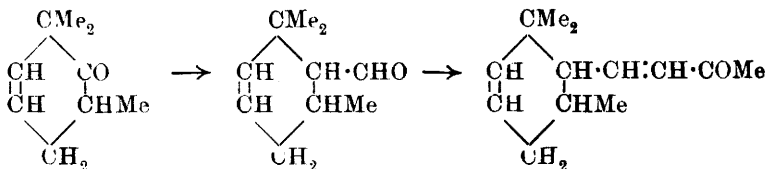
162.5—163.5°, and yields the 3:5:5-triphenylthiazolid-2:4-dione, mentioned in the previous abstract, when boiled with acetic and sulphuric acids.

J. C. W.

Preparation of Benzaldehyde. THE DOW CHEMICAL COMPANY (U.S. Pat., 1272522).—Benzyl bromide is mixed with a solution of sodium nitrate or calcium nitrate, and the mixture is heated at about the boiling point with constant agitation; the benzaldehyde produced is then separated from the aqueous solution of sodium bromide and nitrous acid. The reaction takes place between equimolecular proportions of benzyl bromide and sodium nitrate, and the benzaldehyde is practically a pure product, whereas that produced with benzyl chloride and lead nitrate is always contaminated with benzoic acid.

J. F. B.

Preparation of Polymethylcyclohexenones of the Irone Type. L. RUZICKA (*Helv. Chim. Acta*, 1919, 2, 144—161).—For the synthesis of perfumes of the type of irone, the author argues that it is important to start from compounds in which the ethylene linking in the cyclohexene ring is already fixed, such methods as those described by Merling and Velde, for example (A., 1909, i, 479), being open to question on this point. The conversion of a cyclohexenone of the desired type into irone or a similar compound would be quite a simple matter; thus:



The present communication describes the preparation of two such cyclohexenones, but the yields are so poor that further developments along these lines seem to be useless.

The desired cyclohexenones should be most readily obtained from the corresponding unsaturated dicarboxylic acids, and these from δ -ketonic esters by Reformatzky's method. The chief obstacle is the closing of the ring in the case of the dicarboxylic esters. Two examples are given.

A. Preparation of the δ -Ketonic Esters.— δ -Ketohectic acid may be prepared most readily by the interaction of ethyl sodioacetoacetate and ethyl β -iodopropionate. With suitable apparatus, it may also be obtained by heating dihydroresorcinol with barium hydroxide and water at 150°. A third method, giving poor results, is as follows: fresh ethyl methylenemalonate is treated with ethyl sodioacetoacetate solution at 0°, and the ethyl δ -ketopentane- $\alpha\gamma$ -tricarboxylate so formed, b. p. 198—200°/15 mm., is boiled with dilute hydrochloric acid. The δ -ketohectic acid is readily esterified by boiling with alcohol containing a little hydrogen chloride.

Ethyl δ -keto- α -methylhectoate, b. p. 110—112°/13 mm., and the

free acid, b. p. 157—159°/13 mm., are prepared by the interaction of a solution of ethyl sodioacetoacetate and ethyl methylacrylate, followed by boiling the *ethyl ε-ketohexane-βδ-dicarboxylate* so formed, b. p. 152—156°/12 mm., with hydrochloric acid.

Ethyl *δ-keto-αα*-dimethylhexoate, b. p. 110—115°/13 mm., is obtained from the acid, this being formed by heating methyl 4:6-diketo-2:2-dimethylcyclohexane-1-carboxylate (from mesityl oxide and methyl sodiomalonate) with barium hydroxide and water at 150° (compare Brecht, A., 1898, i, 264).

B. Condensations of the *δ*-Ketonic Esters with Ethyl *α*-Bromo-isobutyrate.—These condensations are brought about by means of zinc turnings, and the lactonic esters are isolated in the usual way. Ethyl *δ-ketohexoate* gives the lactone of *δ-hydroxy-ε-carbethoxy-*

δε-dimethylheptoic acid,
$$\text{CO}_2\text{Et} \cdot \text{CMe}_2 \cdot \text{CMe} \cdot \text{CH}_2 \cdot \underset{\text{O}-\text{CO}-\text{CH}_2}{\text{CH}_2}, \quad \text{m. p.}$$

176—177°. Ethyl *δ-keto-α*-methylhexoate yields the lactone of *δ-hydroxy-ε-carbethoxy-αδε*-trimethylheptoic acid, b. p. 169—171°/12 mm., and the third ester produces the lactone of *δ-hydroxy-ε-carbethoxy-ααδε*-tetramethylheptoic acid, b. p. 170—175°/12 mm.

C. Hydrolysis of the *δ*-Lactonic Esters.—The first two lactones are readily hydrolysed to the esters of unsaturated dicarboxylic acids by boiling them with alcoholic hydrogen bromide, but the third lactone has a very stable ring. *βγ*-Dimethyl-*Δγ*-hexene-*βζ*-dicarboxylic acid, $\text{CO}_2\text{H} \cdot \text{CMe}_2 \cdot \text{CMe} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, from the first lactone, forms stout needles, m. p. 108—109°, gives an *ethyl* ester, b. p. 153—157°/12 mm., and yields acetic, isobutyric, and succinic acids on oxidation with permanganate. *βγ*-Dimethyl-*Δγ*-heptene-*βζ*-dicarboxylic acid, from the second lactone, has m. p. 84—85°, and its *ethyl* ester has b. p. 153—157°/12 mm.

D. Preparation of the Polymethylcyclohexenones.—When the ester of the above hexenedicarboxylic acid is boiled with sodium powder in benzene, it yields a small quantity of *ethyl 4-keto-2:3:3-trimethyl-Δ¹-cyclohexene-1-carboxylate*, most of the material suffering complex condensation. This ester gives *2:3:3-trimethyl-Δ¹-cyclohexen-4-one* on hydrolysis, b. p. 85—90°/12 mm.; *semicarbazone*, m. p. 168—171°. When methylated and then hydrolysed, it also forms *2:3:3:5-tetramethyl-Δ¹-cyclohexen-4-one*, b. p. 90°/12 mm.; *semicarbazone*, m. p. 196—197°.

Displacement of the ethylene linking occurs if the unsaturated dicarboxylic acids are heated with acetic anhydride and then distilled. The hexenedicarboxylic acid yields *3:4:4-trimethyl-Δ¹-cyclohexen-5-one*, b. p. 85—90°/14 mm., *semicarbazone*, m. p. 185—187°, which may be reduced by sodium and alcohol to *1:2:2-trimethylcyclohexan-3-ol*, b. p. 85—87°/15 mm. The heptenedicarboxylic acid yields *3:4:4:6-tetramethyl-Δ¹-cyclohexen-5-one*, b. p. 80—85°/13 mm.; *semicarbazone*, m. p. 178—179°.

J. C. W.

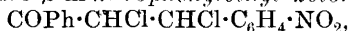
The Reduction of Aromatic Ketones. W. D. COHEN (*Rec. trav. Chim.*, 1919, **38**, 113—131).—In continuation of previous

work (compare this vol., i, 124), the author has studied the reduction of a number of substituted benzophenones by aluminium amalgam in alcohol, and determined the proportions of substituted benzhydrol and benzopinacone formed in each case. The proportion of benzhydrol to benzopinacone is found to depend directly on the velocity with which the pinacone is decomposed in alkaline solution to give the hydrol and the ketone. Thus, then aluminium amalgam is, at the moment of reduction, a slightly alkaline reagent and promotes the secondary reaction, the products of which are dependent on the velocity with which the primary product, the pinacone, is attacked. The course of the reaction in the reduction of benzophenone consists of the preliminary formation of diphenylhydroxymethyl, $\text{CPh}_2\cdot\text{OH}$, which is immediately transformed into pinacone.

o-Chlorophenyl *p*-tolyl ketone, m. p. $99\cdot5^\circ$, is obtained by the condensation of *o*-chlorobenzoyl chloride with toluene in the presence of aluminium chloride. It yields 2-chloro-4'-methylbenzhydrol, m. p. 67° , and 2-chloro-4'-methylbenzopinacone, m. p. $175\text{--}176^\circ$. *p*-Chlorophenyl *p*-tolyl ketone, m. p. 118° , similarly prepared, gives only the corresponding hydrol, m. p. $67\cdot5^\circ$, by reduction in neutral solution, and the pinacone, m. p. 178° , by reduction in acid solution. W. G.

Some Ketone Condensation Reactions. SVEN BODFORSS (*Ber.*, 1919, 52, [B], 142—145).—The author has shown (A., 1917, i, 223; 1918, i, 229) that Widman's reaction (A., 1913, i, 1219; 1916, i, 406; 1917, i, 221) is not a general one for aldehydes. It is of interest, therefore, to ascertain what course the Erlenmeyer reaction will take when derivatives of chloroacetic acid other than the ethyl ester are employed. An alcoholic solution of benzaldehyde ($1\frac{1}{2}$ mols.) and chloroacetanilide cooled in a freezing mixture yields by treatment with sodium ethoxide solution and subsequent acidification with dilute acetic acid $\alpha\beta$ -oxido- β -phenylpropionanilide, $\begin{array}{c} \text{CHPh} \\ | \\ \text{O} \end{array} \text{---} \text{CH}\cdot\text{CO}\cdot\text{NHPh}$, colourless needles, m. p. 142° .

Phenyl $\alpha\beta$ -dichloro- β -*m*-nitrophenylethyl ketone,



colourless crystals, m. p. 148° , is obtained by saturating a glacial acetic acid solution of ω -chloroacetophenone and *m*-nitrobenzaldehyde with hydrogen chloride in the cold, and also by leading chlorine into a solution of phenyl *m*-nitrostyryl ketone in the same solvent.

Cuminaldehyde and acetophenone, condensed by means of methyl-alcoholic sodium methoxide, yield phenyl isopropylstyryl ketone, $\text{C}_6\text{H}_4\text{Pr}^\beta\cdot\text{CH}\cdot\text{CH}\cdot\text{COPh}$, b. p. $225\text{--}227^\circ/15$ mm. (slight decomp.), which forms a dibromide, needles, m. p. $119\text{--}119\cdot5^\circ$.

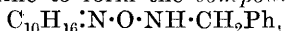
C. S.

Theory of Colour Lakes. Action of Potassium Ferri-cyanide on Alizarin in Alkaline Solution and the Constitution of Hydroxyanthraquinones. OSKAR BAUDISCH (*Ber.*, 1919, 52, [B], 146—147).—A claim of priority over Scholl and Zinke

(this vol., i, 25. Compare also Baudisch, A., 1917, i, 356, 556; Baudisch and Klaus, *ibid.*, i, 331). C. S.

Optically Active Pinene Nitrosochloride, and Synthetic Active Pinene. E. V. LYNN (*J. Amer. Chem. Soc.*, 1919, **41**, 361—368).—In the preparation of the nitrosochloride from pinene by Wallach's method, it is well known that the yield of crystalline product varies inversely with the optical activity of the specimen, whilst the mother liquor remains blue for some time with the most active oils. An obvious suggestion, therefore, is that the active nitrosochlorides are more soluble than the inactive one, but Tilden offered another explanation of the poor yield (T., 1904, **85**, 759—764). By varying the conditions of the experiment, somewhat better yields may be obtained and the active nitrosochlorides actually isolated.

Equal volumes of pinene, ethyl nitrite, and alcohol are mixed and treated at -5° with the requisite amount of hydrogen chloride dissolved in alcohol. Crystals of inactive pinene nitrosochloride are removed after half an hour, and the mother liquor is then diluted with alcohol and left at -10° , when the active modification gradually separates. The dextro-variety was obtained in this instance from American turpentine, and the lævo-modification from Oregon or Canada balsams. Active pinene nitrosochloride crystallises in transparent or cotton-like needles, m. p. $81-81.5^{\circ}$, $[\alpha]_D +322^{\circ}$, and is appreciably soluble in most organic media. It reacts with benzylamine to form the compound



m. p. $144-145^{\circ}$, $[\alpha]_D +92^{\circ}$ in acetone, and with piperidine to give a similar compound, crystallising in rosettes, m. p. 84° , $[\alpha]_D +50^{\circ}$. With alcoholic alkali hydroxide, it reacts to form nitrospinene, and with aniline to give aminoazobenzene and active pinene; b. p. $155-159^{\circ}$, $n_D 1.470$, $[\alpha]_D +53.75^{\circ}$ in 4% alcoholic solution. This "regenerated" *d*-pinene gave an inactive hydrochloride, like the natural product.

The existence of active nitrosochlorides in the mother liquors does not by any means fully account for the poor yields. Even inactive pinene only gives about 50% of the theoretical yield. As the blue solution deposits its colourless crystals, a gas is evolved which Tilden suggested might be nitrous oxide. It is now conclusively proved to be nearly pure nitrogen, and its volume agrees closely with that of the nitrogen unaccounted for. The mother liquor has been briefly examined, and found to be a complex mixture. J. C. W.

Keto-cineole. GUIDO CUSMANO (*Gazzetta*, 1919, **49**, i, 26—38).—When heated with ethyl alcohol, α -terpineol nitrosochloride is converted in satisfactory yield into keto-cineole-oxime, and this with nitrous acid gives quantitatively the pernitroso-compound, from which the free ketone is obtained, also quantitatively, by treatment with concentrated aqueous ammonia (compare Cusmano and Linari, A., 1912, i, 272).

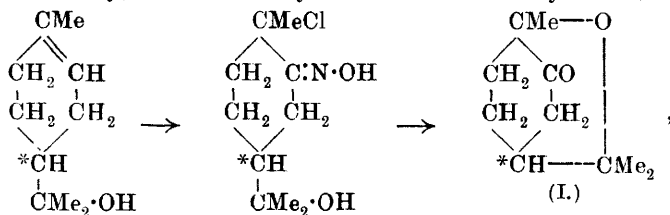
Saturated cyclic ketones containing ten carbon atoms in the molecule and possessing the $\cdot\text{CO}\cdot\text{CH}_2\cdot$ grouping and the general structure of keto-cineole may be divided into two groups: (1) menthoue, tetrahydrocarvone, and tanacetone, and (2) camphor and pinocamphone. All show the same reactions of the carbonyl and of the adjacent methylene group, and opening of the fundamental hexamethylene nucleus between the carbonyl and the neighbouring tertiary (or quaternary) carbon atom is possible in all cases; rupture between the carbonyl and the methylene in addition is, however, possible only with the ketones of the second group. With the latter, which possess a "bridge," keto-cineole must be classed. Keto-cineole exhibits marked physiological activity, which is to be investigated.

Reduction of keto-cineole oxime by means of sodium and boiling amyl alcohol yields as one product an *aminocineole*, which forms a crystalline *platinichloride*, $(\text{C}_{10}\text{H}_{17}\text{O}\cdot\text{NH}_2)_2\cdot\text{H}_2\text{PtCl}_6\cdot 2\text{H}_2\text{O}$, m. p. 233° (decomp.).

Inactive keto-cineole forms shining, white, lamellar crystals, m. p. 42° , and yields a *semicarbazone*, m. p. 220° , and a *phenylhydrazone*, $\text{C}_{10}\text{H}_{16}\text{O}\cdot\text{N}_2\text{HPh}$, m. p. about 160° , which gradually loses phenylhydrazine.

The use of inactive α -terpineol mixed with some of the dextro-rotatory form results in the formation of inactive and active keto-cineole-oximes. The active oxime forms prismatic crystals, m. p. 168° , $[\alpha]_D^{25}$ in methyl alcohol -11.8° . The active keto-cineole forms colourless, lamellar crystals, m. p. about 50° , $[\alpha]_D^{25} = 44.0^\circ$.

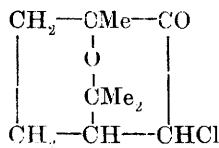
Although keto-cineole contains two asymmetric carbon atoms, the optical activity, as is shown by the scheme of the synthesis,



is due only to the one marked with an asterisk, this being pre-existent in the active α -terpineol. T. H. P.

Halogenated Compounds of Keto-cineole. GUIDO CUSMANO (*Atti R. Accad. Lincei*, 1919, [v], **28**, i, 78—83. Compare preceding abstract).—Keto-cineole is readily converted into monochloro-(or monobromo-)keto-cineole (annexed formula), but further

halogenation results in the formation of derivatives of carvomenthone (tetrahydrocarvone). The structure of the monohalogenated compounds is established by the action of potassium permanganate (three atoms of oxygen per molecule of halogen derivative) or of dilute potassium hydroxide solution, which



converts them into cineolic acid, this reaction being similar to the transformation of analogous camphor derivatives into camphoric acid. When treated with hydrogen bromide in ethereal solution, keto-cineole yields 1:8-dibromocarvomenthone (*loc. cit.*); the latter, and not 1:3:8-tribromocarvomenthone, is also obtained by the action of hydrogen bromide on monobromoketo-cineole under similar conditions, transformation of the cineole "bridge" being accompanied by elimination by reduction of the bromine atom from the methylene group next to the carbonyl.

Monochloroketo-cineole, $C_{10}H_{15}O_2Cl$, forms shining, elongated prisms, m. p. 78° , and volatilises unchanged (compare Cusmano, this vol., ii, 61).

Monobromoketo-cineole, $C_{10}H_{15}O_2Br$, forms transparent, colourless, prismatic crystals, m. p. about 90° , and when volatilised emits an odour of keto-cineole. By bromine (2 atoms per mol.) in chloroform solution, it is converted into a *compound*, which crystallises in nacreous, lamellar crystals, m. p. 143° , and appears to be a tetrabromotetrahydrocarvone, $C_{10}H_{14}OBr_4$. T. H. P.

Digitalis Glucosides. XXXIX. H. KILIANI (*Ber.*, 1919, **52**, [B], 200—205).—After many years of disappointment, the author has now succeeded in degrading a compound of the digitalis series, namely, digitogenic acid (A., 1902, i, 46), to simpler substances which may open up the way to a final elucidation of the composition of the glucosides.

When heated at 100° with ten times its volume of 50% alcohol and concentrated hydrochloric acid in the proportion 25:1, digitogenic acid is hydrolysed to a *lactone*, $C_8H_{12}O_2$ (this may be corrected in the future), m. p. 93° , $[\alpha]_D -79.5^\circ$, and a monobasic *acid*, $C_{20}H_{32}O_6$ (or $C_{20}H_{30}O_6$), which crystallises well from diluted acetic acid with $0.5H_2O$, has m. p. 112° , $[\alpha]_D -79.8^\circ$, and forms a *magnesium* salt with $6H_2O$. J. C. W.

Saponins. I. E. WINTERSTEIN and M. MAXIM (*Helv. Chim. Acta*, 1919, **2**, 195—203).—A short summary of the present knowledge of saponins is given, and attention is directed to the need for more extensive studies of the sapogenins which remain when these glucosides are hydrolysed. For a preliminary investigation of this sort, the authors have chosen the saponins of the horse-chestnut and the soap-berry (*Sapindus saponaria*). These may be isolated as follows. The crushed or powdered material is extracted with ether, then with warm 95% alcohol in the presence of calcium carbonate, and the alcoholic extract is evaporated, diluted with water, and digested with lead hydroxide for several days. After filtering and removing lead from the filtrate, the solution is concentrated in a high vacuum. For the further purification of the saponins, dialysis may be advisable, as the plant material contains a good deal of sucrose.

Horse-chestnut saponin is readily hydrolysed by dilute acids in the cold. *Sapindus* saponin, however, is only partly degraded by

cold acids. It appears to be a mixture of glucosides, which gives a mixture of pentosides when partly hydrolysed ("initial sapogenins"), these being converted into the "end sapogenins" by means of warm acids. A pentoside is also formed when the saponin is left with dilute hydrogen peroxide at 40° for some days. The sugars present include *D*-fructose and *D*-glucose, and rhamnose and arabinose in the ratio 1:2 or 1:3, and the approximate composition of the saponin is roughly 33—35% "end sapogenin," 45% hexoses, and 15% pentoses.

Sapindus saponin may be brominated in methyl-alcoholic solution. The product has just the same foaming power as the original saponin, but is no longer hæmolytic; in fact, it hinders the hæmolytic activities of other saponins.

Only about 6 grams of pure sapogenin can be obtained from 100 grams of the crude saponin. The compound, $C_{18}H_{28}O_3$, has m. p. 319°, forms a mono-acetate, gives a fluorescent dye when condensed with resorcinol, and yields naphthalene derivatives on oxidation.

J. C. W.

Curcumin. PRAPHULLA CHANDRA GHOSH (T., 1919, 115, 292—299).

Tannins. I. Hamameli-tannin. KARL FREUDENBERG (*Ber.*, 1919, 52, [B], 177—185).—Although the constitutions of Chinese and Turkish tannins have been elucidated in all essential points by the work of Fischer and his collaborators (1912—1918), the last remaining problems will evidently require time for their solution, because these naturally occurring amorphous substances are very probably inseparable mixtures of very nearly related polygalloyl-glucoses. Grüttner's hamameli-tannin is, however, a crystalline, and therefore probably individual, substance. With regard to its constitution, the only fact known is that it contains gallic acid and a new sugar (Fischer, A., 1913, i, 1352). Titration shows that there is no free carboxyl group. By treatment with diazomethane in acetone solution, hamameli-tannin yields a friable methyl derivative which yields gallic acid trimethyl ether by hydrolysis with *N*-sodium hydroxide. The prolonged treatment with 5% sulphuric acid required to hydrolyse the tannin also causes changes in the sugar produced. The author has therefore hydrolysed a dilute aqueous solution of the tannin covered with toluene with tannase (the preparation of which is described; dextrose must be removed), and obtained gallic acid and a sugar (calculated as a hexose) in quantities corresponding with the formula of a digalloyl-hexose.

The sugar, which has been obtained only as a yellow, viscous, lævorotatory syrup, has not been identified; it appears to contain a normal chain of six carbon atoms.

C. S.

Formation of Flavone or Coumarone Derivatives from Hydroxychalkones. J. TAMBOR and HANS GUBLER (*Helv. Chim. Acta*, 1919, 2, 101—111).—Tambor has recently developed an easy

method for the synthesis of hydroxyflavones, namely, by the action of alcoholic potassium hydroxide on the dibromides of acetoxychalkones (A., 1916, i, 831), and Oesterle and Kueny have used this process in showing the connexion between homoeriodictyol and luteolin (A., 1917, i, 703). It is now shown, however, that flavones are not always formed, coumarones or coumaranones resulting in some cases. Whether the five- or six-membered oxygen ring is formed seems to depend on the position of the substituents in the aldehyde component of the chalkone.

2':4':2-Trihydroxychalkone (2:4-dihydroxyphenyl 2-hydroxystyryl ketone) (Göschke and Tambor, A., 1912, i, 195) is converted into the *triacetate*, glistening needles, m. p. 170—171°, and the *dibromide* of this, which crystallises in long needles, m. p. 144°, is warmed with alcoholic potassium hydroxide, and thus condensed to 2':4'-dihydroxy-1-benzoylcoumarone, $C_6H_4 \begin{smallmatrix} O \cdot C \cdot CO \cdot C_6H_3(OH)_2 \\ | \\ CH \end{smallmatrix}$

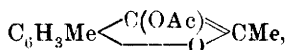
This crystallises as a woolly mass of yellow needles, m. p. 144°, forms a colourless *diacetate*, m. p. 119°, and may be synthesised by the condensation of resorcinol with coumarilic chloride in the presence of aluminium chloride.

The methyl ethers of this coumarone are not easily obtained by direct methylation. They have been prepared by Rap's method for synthesising 1-benzoylcoumarones (A., 1896, i, 303), namely, by the interaction of salicylaldehyde and the mono- or di-methyl ethers of *o*-chlororesacetophenone (A., 1918, i, 395). 2'-Hydroxy-4'-methoxy-1-benzoylcoumarone forms small, lemon-yellow tablets, m. p. 253° (decomp.), and its *acetate* has m. p. 166°; 2':4'-dimethoxy-1-benzoylcoumarone forms colourless prisms, m. p. 102°. Other benzoylcoumarones prepared incidentally, in the same way, include 2'-hydroxy-4':6-dimethoxy-1-benzoylcoumarone, dark yellow tablets, m. p. 253° (decomp.) (*acetate*, m. p. 180°), from 2-hydroxy-3-methoxybenzaldehyde and *o*-chlororesacetophenone monomethyl ether, and 4'-hydroxy-6-methoxy-1-benzoylcoumarone, small, dull yellow prisms, m. p. 189°, from the same aldehyde and *o*-chloro-*p*-hydroxyacetophenone.

The influence of the position of the substituents is further illustrated by another example. 2-Acetoxyphenyl 4-methoxystyryl ketone dibromide yields *p*-methoxybenzylidenecoumaranone when treated with concentrated potassium hydroxide (Herstein and Kostanecki, A., 1899, i, 369), whereas 2-acetoxyphenyl 2-methoxystyryl ketone dibromide gives 2'-methoxyflavone. *o*-Hydroxyacetophenone and *o*-methoxybenzaldehyde are condensed by means of sodium hydroxide to 2-hydroxyphenyl 2-methoxystyryl ketone, yellow needles, m. p. 112°, the *acetate* of which, m. p. 64°, is converted into the *dibromide*, $OAc \cdot C_6H_4 \cdot CO \cdot CHBr \cdot CHBr \cdot C_6H_4 \cdot OMe$, m. p. 101° (decomp.), and then into 2'-methoxyflavone (2'-methoxy-2-phenyl- γ -benzopyrone), m. p. 103°, as indicated (compare A., 1912, i, 486). For comparison with *o*-methoxybenzylidenecoumaranone, this has been synthesised from coumaranone and *o*-methoxybenzaldehyde; it crystallises in straw-yellow prisms, m. p. 175°.

Other *benzylidenecoumaranones*, prepared from suitable aldehydes and coumaranone, are as follows: 2-*hydroxy-3-methoxy*-, yellow needles, m. p. 212° (decomp.) (*acetate*, very pale yellow, silky needles, m. p. 176°); 2:3-*dimethoxy*-, long, pale yellow needles, m. p. 130°; 2:4-*dimethoxy*-, slender, bright yellow needles, m. p. 182—183°; 4-*dimethylamino*-, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{C} \end{smallmatrix} \text{C} \cdot \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$, very dark red needles, m. p. 170—172°. J. C. W.

Alkylated Coumaranones, especially 1:1:4-Trimethylcoumaranone. K. VON AUWERS and H. SCHÜTTE (*Ber.*, 1919, 52, [B], 77—92).—The production of *O*- and of *C*-alkyl derivatives of certain types of coumaranones has been already described (Auwers, A., 1912, i, 484, 486). The parent coumaranones have now been examined. 1:4-Dimethylcoumaranone, b. p. 138—140°/22 mm., which is best purified by distillation (A., 1915, i, 440), yields by acetylation 2-*acetoxy*-1:4-*dimethylcoumarone*,



stout crystals, m. p. 29—30°, b. p. 170·5—171·5°/28 mm., which is converted into 1-chloro- and 1-bromo-1:4-dimethylcoumaranone, respectively, by chlorine or bromine in carbon disulphide solution, and easily undergoes fission by treatment with warm acids, being converted, therefore, by *p*-nitrophenylhydrazine hydrochloride in aqueous-alcoholic solution into 4-hydroxy-*m*-tolyl methyl diketone di-*p*-nitrophenylhydrazone (A., 1918, i, 193).

1:4-Dimethylcoumaranone forms an *oxime*, $\text{C}_{10}\text{H}_{11}\text{O}_2\text{N}$, colourless needles, m. p. 129°. The ketone, which yields chiefly the *O*-methyl derivative by shaking with methyl sulphate and sodium hydroxide solution (A., 1918, i, 27), is converted mainly into 1:1:4-trimethylcoumaranone by boiling with methyl iodide and sodium methoxide solution, or, better, by treatment with sodamide and methyl iodide in ethereal solution; in the former method about 20%, and in the latter about 5%, of the *O*-ether is produced. The *C*-ether is separated by conversion into the semicarbazone. The proof that the new methyl group is attached in position 1 is obtained indirectly by showing that 1:4-dimethylcoumaranone by ethylation and 4-methyl-1-ethylcoumaranone by methylation, as above, yield the same 1:4-*dimethyl-1-ethylcoumaranone*, b. p. 135—135·5°/18 mm., D_4^{20} 1·056, n_D^{20} 1·5359 (*semicarbazone*, colourless needles, m. p. 184—187°). A second proof is furnished by heating 1:1:4-trimethylcoumaranone with sodamide in boiling benzene or toluene, whereby α -*p*-tolyl α -oxyisobutyramide, $\text{C}_6\text{H}_4\text{Me} \cdot \text{O} \cdot \text{CMe}_2 \cdot \text{CO} \cdot \text{NH}_2$, colourless prisms, m. p. 84—85°, is obtained. C. S.

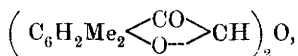
Coumaranones and Hydrindones. KARL VON AUWERS and ELISABETH AUFFENBERG (*Ber.*, 1919, 52, [B], 92—113).—In connexion with the conversion of benzylidene derivatives of substituted

coumaranones into flavonols (Auwers and Pohl, A., 1914, i, 981) and the fission of the furan ring of coumaranones by semicarbazide and certain arylhydrazines (Auwers and Müller, A., 1918, i, 27), the evidence hitherto obtained has allowed certain generalisations to be made regarding the influence of substituents on the stability of the furan ring (Auwers and Müller, *loc. cit.*). To fortify this evidence, the behaviour of a further series of coumaranones towards semicarbazide and towards *p*-nitrophenylhydrazine has been examined. The coumaranone is treated with semicarbazide hydrochloride ($2\frac{1}{2}$ — $3\frac{1}{2}$ mols.) and sodium acetate in aqueous-alcoholic solution at 40—50° for three to four days, or is heated on the water-bath for a few hours with *p*-nitrophenylhydrazine hydrochloride in aqueous-alcoholic solution; according as the product is a mono- or di-semicarbazone or a mono- or di-*p*-nitrophenylhydrazone, the furan ring of the coumaranone has not or has been ruptured. Thus 4-methoxycoumaranone yields the *semicarbazone*, $C_{10}H_{11}O_3N_3$, colourless needles, m. p. 225—226°, 5-methoxycoumaranone yields the *semicarbazone*, $C_{10}H_{11}O_3N_3$, faintly yellow needles, m. p. 213—215°, 3:5-dimethylcoumaranone yields the *semicarbazone*, $C_{11}H_{13}O_2N_3$, colourless needles, m. p. 249—251°, and the *p*-nitrophenylhydrazone, $C_{16}H_{15}O_3N_3$, red needles, m. p. 233°, coumaranone yields *o*-hydroxyphenylglyoxaldi-*p*-nitrophenylhydrazone,

$OH \cdot C_6H_4 \cdot C(=N \cdot NH \cdot C_6H_4 \cdot NO_2) \cdot CH : N \cdot NH \cdot C_6H_4 \cdot NO_2$, brownish-red, crystalline powder, m. p. about 265°, 5-methylcoumaranone yields 2-hydroxy-*p*-tolylglyoxaldi-*p*-nitrophenylhydrazone, m. p. about 260°, 6-methylcoumaranone yields 2-hydroxy-*m*-tolylglyoxaldi-*p*-nitrophenylhydrazone, $C_{21}H_{18}O_5N_6$, brownish-violet, crystalline powder, m. p. about 270°, 5-methoxycoumaranone yields 2-hydroxy-4-methoxyphenylglyoxaldi-*p*-nitrophenylhydrazone, $C_{21}H_{18}O_6N_6$, brownish-violet, crystalline powder, m. p. 264°, and 4-methoxycoumaranone yields 2-hydroxy-5-methoxyphenylglyoxaldi-*p*-nitrophenylhydrazone, reddish-brown, crystalline powder, m. p. 264°. 1:1:4-Trimethylcoumaranone (preceding abstract) yields a *p*-nitrophenylhydrazone, $C_{17}H_{17}O_3N_3$, canary-yellow needles, m. p. 148°. The results confirm the generalisations previously made, to which a fourth is now added, namely, the furan ring of 1:1-dialkylcoumaranones is characterised by its special stability.

Since it is possible that the varying stability of the coumaranones towards ketone reagents may be conditioned by their varying tendency to undergo enolisation, the behaviour of the substances during acetylation and during bromine titration by Meyer's method has been examined. No differences could be detected. All the coumaranones acetylate smoothly (of course, provided there is a hydrogen atom in position 1). Meyer's bromine method shows that the coumaranones in question (that is, coumaranones which do not contain an acyl substituent in position 1 [compare Auwers, A., 1912, i, 484, 1009]) are almost entirely ketonic in the solid state, in the fused state, and even after keeping in alcoholic solution for several days. 5-Methoxycoumaranone yields 2-acetoxy-5-

methoxycoumarone, colourless needles, m. p. 74—76°, by treatment with cold pyridine and acetyl chloride, and 3:5-dimethylcoumaranone yields 2-acetoxy-3:5-dimethylcoumarone, colourless needles, m. p. 65—66°, by boiling with acetyl chloride, and 1-bromo-3:5-dimethylcoumaranone, yellow needles, m. p. 105°, softening at 103°, by treatment with bromine in carbon disulphide solution; the bromo-derivative is converted by sodium carbonate in boiling aqueous acetone into the *ether*,



colourless needles, m. p. 210—212°.

Since α -hydrindones are allied to coumaranones in structure, it is not impossible that they also might be ruptured in the 5-ring by ketone reagents. However, the following hydrindones all react normally with semicarbazide and with *p*-nitrophenylhydrazine: 1-hydrindone yields a semicarbazone, and *p*-nitrophenylhydrazone, $\text{C}_{15}\text{H}_{13}\text{O}_2\text{N}_3$, brownish-red leaflets (from xylene) or orange, crystalline powder (from glacial acetic acid), m. p. 234—235°, 2-methyl-1-hydrindone yields a semicarbazone, colourless, crystalline powder, m. p. 200° with previous softening, and a *p*-nitrophenylhydrazone, brownish-red, microscopic crystals, m. p. 167—168°, 2-phenyl-1-hydrindone forms a semicarbazone, stout crystals, m. p. 211—212°, and a *p*-nitrophenylhydrazone, red crystals and yellow leaflets, both having m. p. 174°, and changeable the one into the other by crystallisation from suitable solvents, 3-phenyl-1-hydrindone forms a semicarbazone, colourless crystals, m. p. 223—225°, darkening at 218°, and a *p*-nitrophenylhydrazone, brick-red crystals, m. p. 220—221°, and 6-methoxy-2-methyl-1-hydrindone, b. p. 148°/10 mm., D_4^{20} 1.116, D_4^{60} 1.1188, n_D 1.55310, n_D 1.55884, n_D 1.57529 at 16.9°, prepared from β -*p*-methoxyphenyl- α -methylpropionyl chloride, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{COCl}$, b. p. 167°/23 mm. (the acid itself, $\text{C}_{11}\text{H}_{14}\text{O}_3$, colourless needles and prisms, m. p. 40°, b. p. 308°, is obtained from ethyl *p*-methoxy- α -methylcinnamate, b. p. 176—177°/15 mm., $D_4^{15.6}$ 1.0894, D_4^{20} 1.085, n_D 1.56213, n_D 1.57009, n_D 1.59339 at 15.6°, which is itself obtained by warming Wallach's ethyl β -hydroxy- β -*p*-methoxyphenyl- α -methylpropionate with phosphoryl chloride), forms a semicarbazone, colourless, crystalline powder, m. p. 215—216°, and *p*-nitrophenylhydrazone, yellow needles, m. p. 163—164°.

Since the hydrindone last mentioned corresponds in structure with 4-methoxy-1-methylcoumaranone, which is most easily ruptured by semicarbazide, it is improbable that any member of the hydrindone series can be ruptured by ketone reagents. None of them exhibits the character of an enol; they cannot be acetylated and do not absorb bromine in the Meyer titration method. Only in one case has the 5-ring of a hydrindone given evidence of instability; 2-phenyl-1-hydrindone, after exposure to air for three months, yields β -deoxybenzoin-*o*-carboxylic acid by auto-oxidation (compare Salway and Kipping, T., 1909, **95**, 116).

C. S.

Spectrochemistry of Coumaranones and of Allied Bicyclic Ketones. K. VON AUWERS (*Ber.*, 1919, **52**, [B], 113—129).—It has been shown (preceding abstracts) that the coumaranones behave as desmotropic substances towards chemical reagents, but in the solid or fused state are almost entirely ketonic. The same conclusion is reached on spectrochemical evidence. For coumaranones of the type $R\langle\overset{\text{CR}'}{\underset{\text{O}}{\text{C}}}\rangle\text{CH}$, the mean values of the specific exaltations are $E\Sigma_a + 0.67$, $E\Sigma_D + 0.72$, $E\Sigma_\beta - \Sigma_a + 37\%$ and $E\Sigma_\gamma - \Sigma_a + 40\%$ (A., 1915, ii, 297), and for those of the type $R\langle\overset{\text{CR}'}{\underset{\text{O}}{\text{C}}}\rangle\text{CR}''$, $E\Sigma_a + 0.87$, $E\Sigma_D + 0.92$, $E\Sigma_\beta - \Sigma_a + 46\%$ and $E\Sigma_\gamma - \Sigma_a + 51\%$. In both cases R' may be alkyl or alkyloxy-groups. When the constants of the coumaranones are calculated on the assumption that these are hydroxycoumaranones, the mean values are $E\Sigma_a + 0.74$, $E\Sigma_D + 0.83$, $E\Sigma_\beta - \Sigma_a + 70\%$ and $E\Sigma_\gamma - \Sigma_a + 82\%$. The exaltations of the refractions agree with those of the coumaranones, but not those of the dispersions.

Coumaranones of the type $R\langle\overset{\text{CO}}{\underset{(-)}{\text{C}}}\rangle\text{CR}''$ must be ketonic. The constants for such are $E\Sigma_a + 1.31$, $E\Sigma_D + 1.41$, $E\Sigma_\beta - \Sigma_a + 89\%$ and $E\Sigma_\gamma - \Sigma_a + 105\%$. The mean values of coumaranones which are capable of enolisation, calculated for the ketonic formula, are $E\Sigma_a + 1.37$, $E\Sigma_D + 1.48$, $E\Sigma_\beta - \Sigma_a + 86\%$ and $E\Sigma_\gamma - \Sigma_a + 97\%$, values which agree with those of the preceding coumaranones. The optical evidence shows, therefore, that all coumaranones as yet examined are ketonic and not enolic in structure. It is also shown spectrochemically that the so-called coumaranonecarboxylic ester is really the enol, 2-hydroxycoumarilic ester, a result which confirms the chemical evidence (A., 1912, i, 1009).

It has been shown (Auwers, A., 1918, ii, 343) that 1-hydrindones and 1-ketotetrahydronaphthalenes exhibit higher exaltations than the homologues of acetophenone structurally allied to them. A further example is presented by 6-methoxy-2-methyl-1-hydrindone (preceding abstract) when compared with 3-methoxyacetophenone. The same phenomenon is seen with heterocyclic ketones containing two ring systems, such as the coumaranones and the chromanones. However, when the carbonyl group in a bicyclic ketone is not attached to the aromatic nucleus, no conjugation occurs, and such substances should be optically normal. This is practically the case with 2-hydrindone and the lactone of *o*-hydroxyphenylacetic acid, for which the values $E\Sigma_a + 0.40$ and $+0.10$, $E\Sigma_D + 0.42$ and 0.11 , $E\Sigma_\beta - \Sigma_a + 14\%$ and $+13\%$, and $E\Sigma_\gamma - \Sigma_a -$ and $+14\%$ respectively are recorded.

C. S.

Guvacine. K. HESS and F. LEIBBRANDT (*Ber.*, 1919, **52**, [B], 206—212. Compare A., 1918, i, 401—403).—In the earlier paper, guvacine was said to be demethylated arecaine, and dihydroguvacine to be identical with *isonipecotinic* acid. Freudenberg, on the other hand (*ibid.*), claimed that guvacine is demethylated arecaine, which would make dihydroguvacine identical with

nipecotinic acid. Hess now agrees with Freudenberg, and with Winterstein and Weinlagen (this vol., i, 171). The discrepancy was due to the properties of *isonipecotinic* acid and dihydroguvacine not being sufficiently well established, and to the fact that a specimen of supposed nipecotinic acid obtained from technical " α -picoline" proved, after all, to be *isonipecotinic* acid.

Guvacine is therefore 1:2:5:6-tetrahydropyridine-3-carboxylic acid, guvacoline is its methyl ester, arecaidine its 1-methyl derivative, and arecoline the methyl ester of this, whilst arecaine is to be cancelled.

The statement in the earlier paper that methylguvacine gives the ethyl ester of guvacine when boiled with alcoholic hydrogen chloride is also in need of correction. The ester arose from unmethylated guvacine, and the ethyl ester of methylguvacine was left in the residue from the distillation.

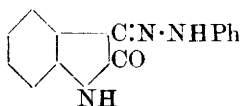
The following table gives the corrected data for the decomposition temperatures of dihydroguvacine (from guvacine regenerated from guvacoline), nipecotinic acid (Ladenburg), and *isonipecotinic* acid, and their hydrochlorides, platinichlorides, and aurichlorides:

	Acid.	HCl.	Pt.	Au.
<i>iso</i> Nipecotinic acid...	328° (1H ₂ O)	280°	245°	213—214° (1H ₂ O)
Nipecotinic acid	249—250°	239—240°	212—213°	195—197°
Dihydroguvacine ...	252°	232—234°	235°	195°

J. C. W.

The Mobility of Hydrogen Atoms in Organic Molecules. Action of Phenylhydrazine on Dioxindoles.

J. MARTINET (*Compt. rend.*, 1919, **168**, 689—691).—Dioxindole and five of its homologues, when acted on by phenylhydrazine, all gave phenylhydrazones of the type of the annexed formula, one molecule of the phenylhydrazine acting as an oxidising agent and the other combining to give the hydrazone.



Thus, in all these cases, a hydrogen atom attached to a carbon atom which was joined to a second carbon atom carrying a double linking was mobile.

W. G.

New Isomerism of the Isatogens. PAUL RUGGLI (*Ber.*, 1919, **52**, [B], 1—8).—It is customary at present to represent isatogens by a quinonoid formula, $C_6H_4 \begin{smallmatrix} C(:O) \\ \diagdown \\ N(:O) \end{smallmatrix} \gg CR$. By heating certain intensely coloured isatogens with alcoholic hydrogen chloride under pressure, the author has obtained less intensely coloured isomerides, for which there appears to be no formula possible except Baeyer's original formula for isatogens, namely, $O \begin{smallmatrix} N-C_6H_4 \\ \diagup \\ CR \cdot CO \end{smallmatrix}$. This formula accords well with the properties of the new isomerides. Thus 6-nitro-2-phenylisatogen, $NO_2 \cdot C_6H_3 \begin{smallmatrix} CO \\ \diagdown \\ NO \end{smallmatrix} \gg CPh$, is converted into

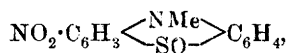
the *isomeride*, $\text{O} \begin{smallmatrix} \text{N} - \text{C}_6\text{H}_3 \cdot \text{NO}_2 \\ \text{CPh} \cdot \text{CO} \end{smallmatrix}$, pale yellow needles, m. p.

151—152°, which remains unchanged in pyridine solution after prolonged exposure to sunlight, forms an *oxime*, $\text{C}_{14}\text{H}_9\text{O}_4\text{N}_3$, yellow crystals, m. p. 180—181° (decomp.), and differs from 2:4-dinitrotolan in being saturated and in being precipitated unchanged by the addition of water to its solution in concentrated sulphuric acid.

Similarly, quinonoid ethyl 2-phenylisatogen-6-carboxylate is converted into an *isomeride*, faintly yellow needles, m. p. 100·5—101·5°, and methyl isatogenate is converted by methyl-alcoholic hydrogen chloride at the ordinary temperature into an *isomeride*, citron-yellow needles, m. p. about 165° (decomp., beginning at about 150°). The latter isomeride in acetone solution containing sodium iodide yields no iodine by acidification, whereas the corresponding quinonoid ester produces a considerable quantity by similar treatment. C. S.

Amino-derivatives of *N*-Methylphenazthionium. F. KEHRMANN and PAULINE ZYBS (*Ber.*, 1919, **52**, [B], 130—141).—The two series of salts of *N*-methylphenazthionium correspond optically with those of phenazthionium, but are considerably less stable (Kehrmann and Sandoz, A., 1918, i, 126). Since it is known that the introduction of electropositive groups, such as alkyl and amino-groups, into the chromogens of "onium" dyes renders the salts more stable towards water, amino-derivatives of *N*-methylphenazthionium have been prepared. The salts, however, are less stable than was anticipated.

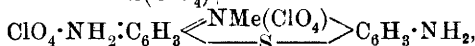
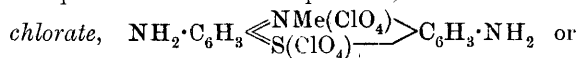
3-Nitro-*N*-methylthiodiphenylamine *S*-oxide,



citron-yellow crystals, m. p. 177°, is obtained by the action of the strongest nitric acid in glacial acetic acid on *N*-methylthiodiphenylamine with cooling and the subsequent addition of water. By using twice the quantity of nitric acid, 3:6-dinitro-*N*-methylthiodiphenylamine *S*-oxide, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{NMe} \\ \text{SO} \end{smallmatrix} \text{C}_6\text{H}_3 \cdot \text{NO}_2$, is obtained, pale yellow prisms, darkening at 280° and decomposing without melting at a higher temperature. The position of the nitro-groups in the *para*-positions to the nitrogen atom is proved by the identity of these nitro-derivatives with the products of the methylation of 3-nitro- and of 3:6-dinitro-thiodiphenylamine *S*-oxide (unpublished observations with Schmajewski). By reduction in alcoholic suspension with stannous chloride and hydrochloric acid, the mono-nitro-derivative yields the colourless stannichloride, and ultimately the *hydrochloride* of 3-amino-*N*-methylthiodiphenylamine, which is extremely unstable on account of its tendency to oxidise. By acetylation with sodium acetate and boiling acetic anhydride, the hydrochloride yields 3-acetyl-amino-*N*-methylthiodiphenylamine,

$\text{NHAc} \cdot \text{C}_6\text{H}_3 \langle \text{NMe} \rangle \text{C}_6\text{H}_4$, colourless needles, m. p. 169°. The acetyl derivative in glacial acetic acid solution is converted by aqueous sodium nitrite into 3-acetyl-amino-N-methylthiodiphenylamine S-oxide, $\text{NHAc} \cdot \text{C}_6\text{H}_3 \langle \text{NMe} \rangle \text{C}_6\text{H}_4$, colourless crystals, decomp. about 235°, and by concentrated aqueous ferric chloride into the ferrichloride, black needles, of the meriquinonoid dye, which is converted by perchloric acid solution into the perchlorate, $\text{C}_{30}\text{H}_{28}\text{O}_{10}\text{N}_4\text{Cl}_2\text{S}_2$, bluish-black needles. When 3-acetyl-amino-N-methylthiodiphenylamine is boiled with 50% sulphuric acid, a cherry-red solution of the meriquinonoid sulphate of the acetylated base is obtained. This becomes orange as the acetyl group is hydrolysed, and ultimately olive-green when the solution is treated with hydrogen peroxide and concentrated sulphuric acid. The olive-green colour of the di-acid salt of the holoquinonoid dye remains at first unchanged after diluting the solution with ice-water, but rapidly becomes dirty blue as the salt hydrolyses.

A similar series of compounds is obtained from 3:6-dinitro-N-methylthiodiphenylamine S-oxide, namely, 3:6-diamino-N-methylthiodiphenylamine dihydrochloride, unstable, colourless needles, and its quinonoid oxidation product, which is isolated as the diperchlorate,



violet leaflets with copper lustre (this salt is not hydrolysed by water), 3:6-diacetyl-amino-N-methylthiodiphenylamine, colourless needles, m. p. 265°, and 3:6-diacetyl-amino-N-methylthiodiphenylamine S-oxide, almost colourless crystals, decomp. about 270°.

C. S.

3:2'-Diquinolyl-2-carboxylic Acid. K. VON IHNATOWICZ and ST. VON NIEMENTOWSKI (*Ber.*, 1919, **52**, [B], 186—188).—2-Cyano-1-benzoyl-1:2-dihydro-3:2'-diquinolyl, $\text{CN} \cdot \text{C}_9\text{H}_6\text{BzN} \cdot \text{C}_9\text{H}_6\text{N}$, honey-yellow crystals, m. p. 210°, is obtained by adding benzoyl chloride to a suspension of 3:2'-diquinolyl in aqueous potassium cyanide solution (compare Reissert, A., 1905, i, 472, 925). When left with concentrated hydrochloric acid for twenty-four to forty-eight hours, it is hydrolysed, and, after neutralisation with sodium hydroxide, yields 3:2'-diquinolyl-3-carboxylic acid, $\text{C}_{19}\text{H}_{12}\text{O}_2\text{N}_2$, microscopic plates of rhombic habit, m. p. 192° (decomp.), which forms a silver salt, exhibits also basic properties, and is converted into 3:2'-diquinolyl by heating.

C. S.

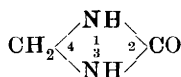
Syntheses of 8:8'-Dihydroxy-5:5'-diquinolyl and a Case of Direct Chlorination by means of Ferric Chloride. L. T. BRATZ and ST. VON NIEMENTOWSKI (*Ber.*, 1919, **52**, [B], 189—194).—When a solution of 8-hydroxyquinoline in about 3% hydrochloric acid is boiled with ferric chloride solution (80 grams in 200 grams of water) for two hours, and then basified with sodium hydroxide

solution and the black precipitate boiled with concentrated aqueous sodium hydroxide, the alkaline solution contains as the chief product of the reaction 5:7-dichloro-8-hydroxyquinoline, the by-products being 5-chloro-8-hydroxyquinoline and the dihydroxydiquinolyl described below.

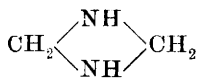
When a 0.3% aqueous solution of 8-hydroxyquinoline at about 40° is treated with ferric chloride solution (35 grams in 100 grams of water), and is then treated as above, 8:8'-*dihydroxy-5:5'-diquinolyl* is obtained in considerable quantity, together with chlorinated products. The formation of the latter is avoided by using ferric sulphate in place of ferric chloride. The dihydroxydiquinolyl, $C_{18}H_{12}O_2N_2$, forms brownish-yellow crystals, m. p. 320—322°, softening at 310°. It is soluble in dilute mineral acids and alkalis, forms a *hydrochloride*, $C_{18}H_{12}O_2N_2 \cdot 2HCl \cdot 2H_2O$, yellow crystals, and *diacetyl* derivative, crystals, m. p. 187°, softening at 180°, and has been prepared from 3:3'-diamino-4:4'-dihydroxydiphenyl by the Skraup reaction. C. S.

Four-membered Cyclic Ureas. I. History and Nomenclature. WILLIAM J. HALE (*J. Amer. Chem. Soc.*, 1919, **41**, 370—378).—In 1869, Schiff obtained condensation products of urea with certain aldehydes, to which he assigned structures based on the ring system, $-N\langle\underset{C}{\rangle}N-$. Since that time, Schiff's theory has been practically abandoned (see, especially, Dixon's work on the formaldehyde reaction, T., 1918, **113**, 238), but other compounds have been discovered which unquestionably contain this heterocyclic system (see Fromm, A., 1893, i, 575; 1906, i, 656; 1913, i, 207; Frerichs and Hartwig, A., 1906, i, 74, 163; Senier and Shepherd, T., 1909, **95**, 504).

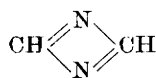
In the further development of the subject which the author contemplates, a proper system of nomenclature for these four-membered ring compounds is desirable. Names with the root "diaz-" would be rational, but in recognition of Fromm's work as the pioneer, and of his terms "alduret" and "keturet," the following arrangement is adopted:



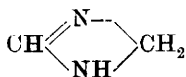
Uretidone



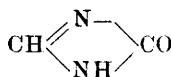
Uretidine.



Urete.



Uretine



Uretone.

J. C. W.

Four-membered Cyclic Ureas. II. Condensation of isoCyanic Acid with a Schiff Base. WILLIAM J. HALE and NORBERT A. LANGE (*J. Amer. Chem. Soc.*, 1919, **41**, 379—388).—When finely powdered potassium cyanate is stirred into a cold

concentrated solution of benzaldazine in glacial acetic acid and the solution is left in a vacuum desiccator over soda-lime for a few days at 0° , 1:4-diphenyluretidone, $\text{CHPh} \begin{smallmatrix} \text{NPh} \\ \text{NH} \end{smallmatrix} \text{CO}$, slowly separates in slender needles, m. p. $224\text{--}225^{\circ}$ (decomp.) (compare the result obtained by Bailey and Moore under other conditions, A., 1917, i, 355). The compound forms a 3-acetyl derivative, m. p. 237° , and yields benzaldehyde and phenylcarbamide on hydrolysis. It cannot, however, be obtained by the condensation of these two substances. If warmed together or mixed with a little alcohol and a few drops of sulphuric acid, they yield *benzylidenebisphenylcarbamide*, $\text{CHPh}(\text{NH}\cdot\text{CO}\cdot\text{NHPh})_2$, m. p. $198\text{--}199^{\circ}$ (decomp.), whilst condensation with alcoholic hydrogen chloride furnishes the *hydrochloride* of *phenyl- α -ethoxybenzylcarbamide*, which is hydrolysed to the free base, $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CHPh}\cdot\text{OEt}$, an amorphous substance, softening at $150\text{--}155^{\circ}$, when its alcoholic solution is poured into water.

Benzylidene-ethylamine reacts with isocyanic acid in quite a different manner; no crystals separate, but if the acetic acid is removed by a current of steam, 4:6-diketophenyl-1-ethylhexahydro-1:3:5-triazine, $\text{CHPh} \begin{smallmatrix} \text{NEt}\cdot\text{CO} \\ \text{NH}\cdot\text{CO} \end{smallmatrix} \text{NH}$, may be isolated in clusters of needles, m. p. 226° .

Staudinger has already directed attention to the similarity between carbimides and ketens with respect to their reactions with unsaturated compounds (A., 1917, i, 666), and it is noteworthy that he has found the same kind of divergence between benzylidene derivatives of aromatic and aliphatic amines as that illustrated above (A., 1910, i, 586). J. C. W.

Diacetyлиндigotin. D. VORLÄNDER and JOHANNES VON PFEIFFER (*Ber.*, 1919, 52, [B], 325—329).—Proof is adduced that the acetyl groups in diacetyлиндigotin are attached to nitrogen, which helps to explain why the compound differs so widely from indigotin in colour.

Indoxylic acid, prepared by fusing the sodium salt of phenylglycine-*o*-carboxylic acid with sodium hydroxide, is heated with acetic anhydride at $90\text{--}100^{\circ}$, and thus converted into *N*-acetyl-indoxyl (A., 1901, i, 563). The position of the acetyl group follows from the fact that acetylanthranilic acid is formed if the compound is boiled with an excess of potassium permanganate in acetone. Diacetyлиндigotin is formed intermediately, and it can be prepared conveniently in this way if an excess of permanganate is avoided. It crystallises from benzene in red prisms or pyramids, m. p. $245\text{--}250^{\circ}$, and yields a comparatively soluble form of indigotin when boiled with an acetic acid solution of hydrogen chloride.

O-Acetylindoxyl (*ibid.*) yields indirubin when oxidised by perhydrol in acetic acid solution.

Although indoxyl yields the two acetyl derivatives, indigo-white

only yields one diacetyl derivative. This is the *N*-isomeride, for it may be oxidised to acetylanthranilic acid.

Diacetyl-o-dimethylindigo-white, $C_{22}H_{20}O_4N_2$, obtained by acetylating the alkaline solution of "*o*-tolylindigo-white," crystallises in white tablets, m. p. 245—248°, and may be oxidised by nitrogen trioxide fumes to *diacetyl-o-dimethylindigotin*, orange-yellow tablets, m. p. 178° (decomp.). The corresponding *dibenzoyl* compound forms yellow crystals, m. p. 175° (decomp.). J. C. W.

Mercury Mercaptide Nitrites and their Reaction with the Alkyl Iodides. IV. Chain Compounds of Sulphur (*continued*). PRAFULLA CHANDRA RÂY and PRAFULLA CHANDRA GUHA (T., 1919, 115, 261—271).

Dihydroxydihydroglyoxalines and their Conversion into Glyoxalines. II. OTTO DIELS and CARRY SALOMON (*Ber.*, 1919, 52, [B], 43—51. Compare Diels, A., 1918, i, 448).—Further experiments have been undertaken to characterise and to confirm the constitution of 3:4-oxido-2-phenyl-4:5-dimethyl-3:4-dihydroglyoxaline (*loc. cit.*). It reacts additively with acetyl chloride to form a compound, $C_{18}H_{15}O_2N_2Cl$, colourless crystals, m. p. 148°, with benzoyl chloride to form the compound, $C_{18}H_{17}O_2N_2Cl$, crystals, m. p. 162°, both of which are stable, with phenylcarbimide in pyridine solution to form the compound, $C_{18}H_{17}O_2N_3$, colourless crystals, m. p. 140°, and with ethylcarbimide in benzene solution to form the compound, $C_{14}H_{17}O_2N_3$, crystals, m. p. 116—118°. It is converted into 2-phenyl-4:5-dimethylglyoxaline by anhydrous ethylamine in benzene solution at 160°, or more smoothly by phenylhydrazine at 200—210°. C. S.

peri-Naphthylenediamine and Selenious Acid. O. HINSBERG (*Ber.*, 1919, 52, [B], 21—28).—The reaction studied by Sachs (A., 1909, i, 426) has been more thoroughly examined. *peri*-Naphthylenediamine (2 mols.) dissolved in pyridine is treated with a solution of selenious acid (1 mol.) in aqueous pyridine, whereby *dihydrodi-peri-naphthaselendiazole*, $C_{10}H_6 \begin{smallmatrix} \text{NH} \\ \text{NH} \end{smallmatrix} \text{Se} \begin{smallmatrix} \text{NH} \\ \text{NH} \end{smallmatrix} C_{10}H_6$, is obtained after the addition of water. It forms yellowish-red flocks, m. p. 120°, and is oxidised very easily, even by air, to *di-peri-naphthaselendiazole*, $C_{10}H_6 \begin{smallmatrix} \text{N} \\ \text{NH} \end{smallmatrix} \text{Se} \begin{smallmatrix} \text{NH} \\ \text{N} \end{smallmatrix} C_{10}H_6$, brown, crystalline powder, m. p. above 300°, which is very sparingly soluble in all solvents except pyridine (*hydrochloride*, blackish-violet needles). *Di-peri-naphthaselendiazole* is decomposed by zinc dust, glacial acetic and concentrated hydrochloric acids on the water-bath, yielding hydrogen selenide and 1:8-naphthylenediamine, and is oxidised by ferric chloride and hydrochloric acid, yielding a black powder, decomp. above 300°. the nature of which has not been ascertained, but it is probably identical with the product obtained from equal molecular quantities of selenic acid and

1:8-naphthylenediamine by warming in dilute acetic acid solution on the water-bath.

The bearing of the preceding results on the author's theory of the structure of the selenium atom (A., 1918, ii, 106) is discussed. C. S.

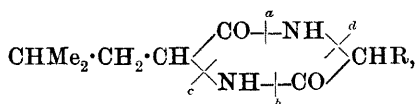
Distillation of Egg Albumin under Reduced Pressure.

AMÉ PICTET and MARC CRAMER (*Helv. Chim. Acta*, 1919, 2, 188—195).—The tar obtained by the dry distillation of animal matter contains substances like aniline, pyridine, and quinoline which bear no relationship to the amino-acids of the proteins. The question arises, therefore, whether the protein complexes contain such atomic groupings, hitherto unrecognised, or whether these compounds are formed by the pyrogenic transformations or condensations of the primary decomposition products. In the hope of throwing some light on the problem, the authors have distilled 4 kilos. of egg-albumin under a pressure of 20—22 mm., but with little success.

Up to 70°, the only product is water; at about 150°, a brisk evolution of gas commences, mostly soluble in sodium hydroxide or dilute sulphuric acid; towards 220°, a yellow oil begins to distil, but at 350° distillation ceases, a very porous and light coke being left behind. The relative proportions of the products are as follows: water, 30%; organic compounds dissolved in this water, 6%; insoluble oil, 9%; coke, 32%; gas and losses, 23%.

The organic compounds are entirely soluble in ether, and can be differentiated into acidic, basic, and neutral fractions. Acetic, propionic, *n*-butyric, and succinic acids may be detected in the first fraction, but no aromatic acids. The bulk of the bases distils at about 175°, and appears to consist of a single primary *amine* of the formula C_6H_5N . It is a very mobile oil, which does not form a diazonium salt, but liberates benzene and nitrogen when warmed with nitrous acid. It is suggested, therefore, that the base may be a dihydroaniline of the formula $NH_2 \cdot CH < \begin{smallmatrix} CH_2 \cdot CH \\ CH=CH \end{smallmatrix} > CH$. It forms a *picrate*, m. p. 185°, and may be acetylated or benzoylated. Pyrrolic bases of higher boiling points are also present.

The chief product of the distillation is found among the neutral substances. It is *isohexoamide*, $CHMe_2 \cdot CH_2 \cdot CH_2 \cdot CO \cdot NH_2$, m. p. 120°. The isolation of this amide has important consequences, since it throws light on the origin of the *isohexonitrile*, which is one of the principal constituents of animal oil (Weidel and Ciamician, A., 1880, 403), and also links this nitrile with leucine, the main product of hydrolytic cleavage, in a common stock, namely, a diketopiperazine ring substituted by an *isobutyl* radicle. Thus, in the formula



cleavage at *a* and *b* results in the formation of leucine, and at *c* and *d* in the production of *isohexoamide*. The neutral fraction contains other amides of fatty acids and compounds of the indole series, including indole itself, which has not been reported in animal oil.

It was expected that the aqueous portion of the distillate would contain *lævoglucosan* if egg-albumin contains a glucose grouping, but no trace of the substance could be detected. J. C. W.

Compressibility of Aqueous Solutions of Casein and Peptone. SVEN PALITZSCH (*J. Amer. Chem. Soc.*, 1919, **41**, 346—351, and *Compt. rend. Lab. Carlsberg*, 1919, **14**, 14—20).—The compressibility, hydrogen-ion concentration, viscosity, specific volume, and density of acid casein solutions, alkaline casein solutions, and peptone solutions have been measured for a series of concentrations at 20°. The compressibilities were measured over the range 100—300 megabars. The compressibility of casein solutions decreases with rising concentrations, and very nearly to the same extent in weakly acid and in weakly alkaline solutions. The compressibility of peptone solutions also decreases, even more markedly, with rising concentration. For the concentration of 10 grams in 100 grams of water, the compressibility of acid casein solution is 40.6×10^{-6} , of alkaline casein solution 40.5×10^{-6} , and of a peptone solution 39.0×10^{-6} . J. F. S.

Nuclein Metabolism. VI. The Cleavage of Nucleotides by means of Hot Aqueous Picric Acid Solutions. Isolation of Crystalline Cytidine-phosphoric Acid. S. J. THANNHAUSER and G. DORFMÜLLER (*Zeitsch. physiol. Chem.*, 1919, **104**, 65—72).—The triphosphonucleic acid obtained from yeast-nucleic acid by hydrolysis with ammonia was further hydrolysed by treatment with hot picric acid solution. From the reaction mixture, a crystalline, brucine salt of cytidine-phosphoric acid was isolated,

$C_9H_{14}O_8N_3P(C_{23}H_{26}O_4N_2)_2$,
m. p. 180—182°. This yielded the free cytidine-phosphoric acid, $C_9H_{14}O_8N_3P$, in a crystalline condition, monoclinic-sphenoidal crystals, m. p. 227°, $[\alpha]_D^{20} = +23.43^\circ$. The two triphosphonucleic acids previously described (A., 1918, i, 47) were submitted to the picric acid hydrolysis. Both yielded the brucine salt of cytidine-phosphoric acid, but only from the *l*-triphosphonucleic acid, m. p. 205°, was the free cytidine-phosphoric acid isolated in the crystalline condition. The inactive triphosphonucleic acid, m. p. 185—187°, is therefore not regarded as a pure substance.

A mixture of uridine-phosphoric acid and cytidine-phosphoric acid may be obtained by hydrolysis of yeast-nucleic acid with picric acid, and the two products may be separated by careful fractional recrystallisation of their brucine salts. J. C. D.

Absorption of Water by Gelatin. EDITH B. SHREVE (*J. Franklin Inst.*, 1919, **187**, 319—337).—The amount of water

absorbed by a gelatin jelly invariably increases with rise of temperature. Since the absorption is accompanied by development of heat, and contraction, Le Chatelier's theorem would require a decreasing water absorption for increasing temperature; it is suggested that the apparent discrepancy is due to the very slow rate of the reaction, equilibrium not being reached before decomposition of the gelatin begins. Hofmeister's results are confirmed, the amount of absorption in some salt and other solutions being less than in water, but greater in other solutions; if, however, the jellies are made up with these solutions instead of with water, the amount of water absorption is in all cases greater than for a jelly made with water only. The bearing of this result on biological conclusions drawn from imbibition experiments is discussed. [See also *J. Soc. Chem. Ind.*, 1919, 297A.] B. V. S.

The Influence of Saponin on the Action of Lipases. A. L. FLOHR (*Arch. Néerland. physiol.*, 1919, **3**, 182—189).—Solutions of saponin activate pancreatic lipase, the influence exerted increasing with the concentration of the saponin up to 2% and then decreasing, using equal volumes of oil and saponin solution. The curves showing these results are analogous to those representing the variation of surface tension of saponin solutions with concentration.

On the other hand, saponin exerts an inhibiting action on the lipase of ricin, the influence increasing steadily with the concentration of the saponin. W. G.

Preparation of Primary and Secondary Arsanilic Acids.

PHILIP ADOLPH KOBER and WALTER S. DAVIS (*J. Amer. Chem. Soc.*, 1919, **41**, 451—458).—The preparation of the so-called primary arsanilic acid was first described by Béchamp in 1863, but the details of the processes which are in use on the large scale, are comparatively secret. The authors have now discovered a simple method for making either the primary or secondary arsanilic acid in a pure state (compare this vol., i, 182).

p-Aminophenylarsinic Acid.—1000 C.c. of technical arsenic acid (76%) are concentrated to 100% by heating at 120—140° for twelve to fifteen hours, then cooled, and stirred into 1400 c.c. of dry, ice-cold aniline. The arsenate so formed (aniline:acid, 3:2) is ground to a powder, and then 200 grams of it are stirred at 160° until molten, and finally heated under reflux for one to one and a-half hours at 160—170° and for one hour at 180—185°. After cooling somewhat, 225 c.c. of 6*N*-sodium hydroxide and 225 c.c. of water are added, when the unchanged aniline is run off and the aqueous layer is shaken with kaolin or kieselguhr, and filtered. The clear solution is mixed with 100 c.c. of 6*N*-hydrochloric acid, and then small portions are tested to see how much more acid is required to cause the complete precipitation of the arsanilic acid. When this has been added, the almost solid mass is filtered, washed by suspending it in 200 c.c. of water, and filtered again.

Di-p-aminophenylarsinic acid, $\text{OH}\cdot\text{AsO}(\text{C}_6\text{H}_4\cdot\text{NH}_2)_2$.—56.4 C.c. of commercial arsenic acid and 1500 c.c. of aniline are heated at 230° in a flask fitted with an inlet tube reaching to the bottom and a condenser, a current of air being drawn through the liquid to ensure good mixing. When about 1200 c.c. of aniline have distilled over, the product is cooled, shaken with 3*N*-sodium hydroxide, and the aqueous layer is then agitated with infusorial earth and filtered. The solution is acidified by 3*N*-acetic acid, and the crude *sec.*-arsanilic acid which separates is purified by dissolving in 3*N*-alkali, removing any aniline by a current of steam, and then adding acetic acid, first until a small precipitate of coloured products is formed, and finally until the acid is completely reprecipitated.

J. C. W.

Preparation of Sodium *p*-Hydroxyphenylarsinate. JAMES B. CONANT (*J. Amer. Chem. Soc.*, 1919, **41**, 431—435).—The preparation of *p*-hydroxyphenylarsinic acid from phenol and arsenic acid represents a first stage in the synthesis of "salvarsan," but little has been published about the reaction beyond the notes of the German patent (A., 1909, i, 279). It is now stated that the best results, giving a yield of about 21.5%, are obtained by heating a well-stirred mixture of phenol and a syrupy arsenic acid corresponding with the formula H_3AsO_4 , at 147 — 157° , for three hours. An excess of acid is used amounting to 10% of the theoretical requirement, and practically nothing but a small quantity of water is lost during the process. The isolation of the sodium salt of the product is best performed as follows. The aqueous solution of the crude acid is filtered from tar, mixed with barium hydroxide until the brown colour begins to change to pink, and then extracted several times with ether to remove tarry matter. More barium hydroxide is then added until a test portion, after rendering it alkaline and filtering, shows the presence of barium ions, when the solution is made just alkaline by the addition of sodium hydroxide, and filtered. The excess of barium is removed by sodium sulphate, and the filtrate evaporated to a red syrup. Impurities are now finally removed by adding sulphuric acid until the colour becomes yellow, when they separate as a viscous, brown oil. The clear solution is then neutralised again and evaporated, a mixture of sodium sulphate and *p*-hydroxyphenylarsinate being obtained. If desired, the latter salt can be extracted by means of alcohol and crystallised.

The next step in the synthesis of "salvarsan" is the nitration of the *p*-hydroxyphenylarsinic acid. For this purpose, the above mixture of sodium salts is quite suitable, but it must be roughly analysed before use. This can be done by taking advantage of the fact that the arsenic acid is converted into tribromophenol on the addition of bromine water. In the nitration, the crude salt, dried at 100° , is stirred into about half its weight of sulphuric acid at 0° , and the nitrating mixture, containing one equivalent of nitric acid, is slowly added. The temperature is allowed to rise gradu-

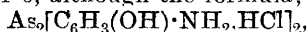
ally to 10°, when the mixture is diluted and the nitro-compound filtered next day.

J. C. W.

Arsenical Compounds. WALTER A. JACOBS, WADE H. BROWN, MICHAEL HEIDELBERGER, and LOUISE PEARCE (Amer. Pats. 1280119—1280223 and 1280225—1280227).—Several derivatives of *N*-phenylglycine-*p*-arsinic acid are described in which the aromatic nucleus containing the arsenic radicle is connected with the α -amino-group of an α -aminoacylamino-side-chain. These compounds are powerful agents in the treatment of trypanosomal and spirochaetal infections. The general methods of preparation consist in treating the sodium salt of *p*-aminophenylarsinic acid with amides, ureides, or anilides of halogenacetic acids, or by treating the methyl ester of *N*-phenylglycine-*p*-arsinic acid with an amine. U.S. Pat. 1280119 relates to amides of *N*-phenylglycine-*p*-arsinic acid or substituted derivatives of the general formula $-\text{NH}\cdot\text{CHR}\cdot\text{CO}\cdot\text{NR}'/\text{R}''$, where R is alkyl, aryl, or hydrogen, and R' and R'' are alkyl or hydrogen. 1280120 relates to *N*-phenylglycine- β -methylureide-*p*-arsinic acid, or generally to derivatives having the side-chain $-\text{NH}\cdot\text{CHR}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NR}'/\text{H}$, in which R and R' are alkyl, aryl, or hydrogen. 1280122 relates to *m'*-amino-phenol-*N*-phenylglycine-*p*-arsinic acid, or generally to derivatives with the side-chain $-\text{NH}\cdot\text{CHR}\cdot\text{CO}\cdot\text{NHAr}$, in which R is alkyl, aryl, or hydrogen, and Ar is an aromatic radicle with or without substituted groups. 1280122 relates to arsenoxides containing the group $-\text{As}=\text{O}$, obtained by the action of mild reducing agents, such as sulphurous acid, on the amides and anilides specified above. 1280123 relates to arsenophenylglycinebisarylamides, obtained by the action of powerful reducing agents on the anilides specified above, whereby two molecules of the anilide unite together, by condensation and reduction, through the bond $-\text{As}=\text{As}-$. These are formed by the action of hypophosphorous and hydriodic acids on the corresponding arsinic acids or arsenoxides; they have a more powerful therapeutic effect than the arsinic acid derivatives. 1280125 relates to readily soluble sodium salts of the above ureides. 1280126 to readily soluble sodium salts of the above anilides, and 1280127 to readily soluble hydrochloric or other acid salts of the above arsenoaryl condensation derivatives, the salt-forming acid being attached to the α -amino-groups of the side-chains in the *para*-position to the arsenic.

J. F. B.

Preparation of Arsphenamine [Salvarsan]. PHILIP ADOLPH KOBER (*J. Amer. Chem. Soc.*, 1919, **41**, 442—451. Compare this vol., i, 183).—The percentage of arsenic in salvarsan is generally found to be about 31·6, although the formula,



requires 34·2%. The difference is usually ascribed to the presence of two molecules of water, although the drug, as prepared by Ehrlich and Berthelm's method (A.. 1912, i. 523), is actually precipitated by methyl alcohol and ether, and these authors have shown that it contains one molecule of methyl alcohol. Kober is

of the opinion that the serious fluctuations in the toxicity of the various preparations, about 50% of which have to be rejected, are largely due to the use of methyl alcohol and ether, and has therefore designed a method for preparing the drug in which no use of these physiologically dangerous and inflammable solvents is made.

A solution of 85 grams of crude nitrohydroxyphenylarsinic acid in 290 c.c. of 2*N*-sodium hydroxide and 1700 c.c. of water is stirred into a solution of 220 grams of magnesium chloride and 1100 grams of sodium hyposulphite in 5500 c.c. of water. The mixture is kept at below 40° until the small amount of suspended impurities seems to be about to settle, when it is rapidly filtered, and the solution kept at 50—60° for two hours or so until the diaminodihydroxyarsenobenzene is deposited. The yellow base is washed with ice-cold water, suspended in 400 c.c. of water, and dissolved in 2*N*-sodium hydroxide, 150 c.c. being sufficient as a rule, all the liquids being cooled to 0°. The solution is then filtered through an anaerobic filter, mixed with 150 c.c. of hydrochloric acid (1:1), and then made up to 1700 c.c. The hydrochloride is finally "salted out" by slowly stirring the solution into 3250 c.c. of hydrochloric acid (1:1), and is dried in a vacuum desiccator over calcium chloride and sodium hydroxide.

Obtained in this way, salvarsan is a pale greyish-white powder containing 1 or 2H₂O, according to the drying, and charring at about 180°. It is less hygroscopic, and therefore more stable, than the ordinary preparations, and has a low grade of toxicity.

A summary of characteristic tests for salvarsan is given.

J. C. W.

Organo-chromium Compounds. F. HEIN (*Ber.*, 1919, 52, [B], 195—196).—By the action of magnesium phenyl bromide on anhydrous chromic chloride or chromyl chloride is obtained, together with other chromium phenyl compounds (as yet unexamined), an orange, amorphous substance which appears to be *chromium pentaphenyl bromide*, CrPh₅Br. It is not attacked by water, but is decomposed by acids, forms a *mercurichloride*, CrPh₅Br.HgCl₂, and has in boiling chloroform a molecular weight corresponding with its formula.

C. S.

Physiological Chemistry.

The Sugars of the Blood. J. W. BEST (*Arch. Néerland. physiol.*, 1919, **3**, 222—266).—The blood of oxen and of horses, taken in the absence of digestion, contains 0.057—0.065% of dextrose, 0.002—0.005% of lactose, and <0.006 —0.012% of an unknown sugar. Galactose, sucrose, melibiose, maltose, and isomaltose are

not present, or, if present, only in quantities less than 0.001%. The unknown sugar is formed by condensation from one or two molecules of a pentose, and contains about twelve atoms of carbon. It gives a phenylosazone, m. p. 181—182°, which from its crystalline form, solubility, and m. p. resembles the osazine of Cumming's sugar (compare *Proc. Roy. Soc.*, 1909, **81**, 374). The sugar is not attacked by either *Saccharomyces cerevisiae*, or emulsin, or the yeast which ferments lactose. It is dextrorotatory. It is not hydrolysed by boiling with dilute mineral acids, or at least only very slowly. The sugar exists as such in the blood, and is not formed during the hydrolysis of the gum of the blood.

The blood of human beings taken in the morning, eleven to sixteen hours after the last meal, contains 0.047—0.082% of dextrose, the residual reduction being equal to 0.019—0.031%, of which half is due to substances precipitable by phosphotungstic acid. Of the remainder, about 0.013% is due to the presence of the unknown sugar described above. Examination of the phenylosazones from the blood sugars before and after fermentation indicates the presence of lactose in human blood, and in one case, that of a woman, thirty-six weeks in pregnancy, 0.006% was found.

W. G.

Hæmocyanin. ERNST PHILIPPI (*Zeitsch. physiol. Chem.*, 1919, **104**, 88—94).—Hæmocyanin is very sensitive to acids. Snails' blood is immediately decolorised by the addition of small quantities of oxalic acid. After treating snails' blood with potassium hydroxide, a product was isolated which contained 7.0% of copper and gave an intense pyrrole reaction. The presence of manganese in the blood of *Pinna squamosa* is confirmed.

J. C. D.

The Effect of Acetone and of β -Hydroxybutyric and Acetoacetic Acids on the Blood Catalase. W. E. BURGE (*J. Biol. Chem.*, 1919, **37**, 343—347).—Introduction of doses of 5 grams per kilo. of 30% solutions of acetone, acetoacetic acid, and β -hydroxybutyric acid into the upper part of the intestines of rabbits produced a rise in the catalase content of blood taken from the jugular vein. Measurements of the catalase present in blood taken from the liver and the portal and jugular veins before and after the administration of these substances in this manner indicate that they stimulate the liver to an increased output of the enzyme. The increased oxidation in diabetes is attributed to the increased production of catalase resulting from such stimulation of the liver.

J. C. D.

The Mechanism of the Action of Fats in the Utilisation and Assimilation of Proteins. F. MAIGNON (*Compt. rend.*, 1919, **168**, 626—629. Compare A., 1918, i, 416).—The author reasserts his views as to the part played by the fatty acids in the building up of specific proteins in the body from the amino-acids arising from the ingested proteins (compare this vol., i, 185).

W. G.

Growth. XI. The Growth, and Senescence of White Mice fed upon Pituitary (Anterior Lobe) Tissue, Tethelin, Egg Lecithin or Cholesterol. T. BRAILSFORD ROBERTSON and L. A. RAY (*J. Biol. Chem.*, 1919, **37**, 393—426).—The results previously reported (A., 1916, i, 350, 690) dealt with the influence of these substances on the growth of mice up to the sixtieth week of life. The present paper records extended observations which cover the whole life-period of the animals. Generally speaking, the results confirm the conclusions announced in the earlier reports. The substances administered to the animals influenced the growth process in the way that catalysts influence chemical reactions, that is, by affecting the velocity with which the equilibrium is attained without affecting the equilibrium itself. J. C. D.

Growth. XII. The Influence of Pituitary Gland (Anterior Lobe) Tissue, Tethelin, Egg Lecithin, and Cholesterol on the Duration of Life of the White Mouse. T. BRAILSFORD ROBERTSON and L. A. RAY (*J. Biol. Chem.*, 1919, **37**, 427—442).—The mean duration of life of mice which have received pituitary tissue, lecithin, or cholesterol lies within normal limits. Those which had received tethelin, the growth-accelerating substance isolated from the anterior lobe of the pituitary gland, showed a greatly extended duration of life. Male mice which had received tethelin continuously showed a duration of life which exceeded the normal by ninety-nine days, whilst in female mice which had received tethelin intermittently in three periods of one month each prior to the thirtieth week, the increased duration of life was eighty-one days. J. C. D.

Growth. XIV. Further Experiments on the Influence of Tethelin on the Growth of the White Mouse. T. BRAILSFORD ROBERTSON and L. A. RAY (*J. Biol. Chem.*, 1919, **37**, 455—463. Compare A., 1916, i, 356, 690).—Discontinuous administration of tethelin will produce the characteristic deformations of the growth curve of white mice. The same result was observed to follow a single relatively brief period of administration, namely, 4 mg. of tethelin per day for eight weeks only, from the fourth to the twelfth week of life. The concavity in the curve of growth is believed to be the expression of preliminary retardation preceding sexual maturity, followed by a secondary or compensatory acceleration accompanying and succeeding sexual maturity. The previous opinion, which held that both acceleration and retardation were directly due to tethelin, is now modified in that only the retardation is believed to be due to that substance, the acceleration being due to compensatory factors which develop in the animal itself in response to the abnormal dosage of the active principle of the anterior lobe of the pituitary body. The direct action of tethelin would thus appear to consist exclusively, so far as the whole animal is concerned, of retardation of growth. J. C. D.

Milk Coagulation and the Physical Condition of Milk Curd. O. ALLEMANN [with H. SCHMIDT] (*Kolloid Zeitsch.*, 1919, **24**, 27—42).—A number of experiments on the solidity of milk curds have been made in connexion with the manufacture of cheese. It is shown that the solidity of rennet curd is directly proportional to the time which has elapsed since coagulation, and inversely proportional to the time of coagulation. The solidity is proportional to the acidity of the mixture. The solidity of the milk curd is increased by the addition of potassium chloride in strict proportion to the amount of salt added. With increasing temperature, the solidity increases up to a maximum, but above 41—42° it decreases rapidly. The solidification of the curd is a continuation of the coagulation process, and it takes place according to the ordinary coagulation laws. The solidity is dependent on the individuality of the animal from which the milk was taken, and is constant over long periods of time. Sudden changes in the solidity relationships can occur; these are the result of weather changes and physiological conditions, and after a short time the solidity relationships return to their normal values.
J. F. S.

The Forms of Nitrogen in Protein-free Milk. CORNELIA KENNEDY (*J. Amer. Chem. Soc.*, 1919, **41**, 388—393).—The so-called protein-free milk is prepared as follows: 40 litres of centrifuged milk, diluted with 8 litres of water, are mixed with a little more than the required amount of hydrochloric acid to cause the formation of a curd, filtered through cheesecloth, the filtrate is boiled for half a minute, cooled, filtered through paper pulp, and the solution neutralised with sodium hydroxide and evaporated to dryness at 60—70°. An examination of the distribution of nitrogen in five samples of such milk, obtained from the same herd at different times, has been made, with the following results: (1) the nitrogenous substances present vary in composition; (2) considerable quantities of proteins or peptides of high molecular weight are still present for there is a great increase in the amount of amino-nitrogen after hydrolysis or tryptic digestion; (3) nearly half of the nitrogenous material is precipitated by mercuric nitrate or phosphotungstic acid, the latter agent removing only non-amino-nitrogen.
J. C. W.

Action of 10 per cent. Thymol-Chloroform Preservative on the Chlorine Content of Urine. J. O. HALVERSON and J. A. SCHULZ (*J. Amer. Chem. Soc.*, 1919, **41**, 440—442).—A solution of thymol in chloroform is being widely used as a preservative for specimens of urine. Its influence on the content of inorganic chlorine has therefore been studied in the case of six alkaline specimens of cow's urine, stored at about freezing point for nearly two years, and sixteen specimens of acidic urine from swine, kept at the ordinary temperature for four to twenty-one days. No variations outside the limits of analytical errors were encountered.
J. C. W.

Cystine of Urine and of Urinary Calculi. EMIL ABDERHALDEN (*Zeitsch. physiol. Chem.*, 1919, **104**, 129—132. Compare A., 1907, i, 476).—The cystine derived from the hydrolysis of hair and nails of a cystinuric patient was found to be identical with that present in the urine. Three cystine calculi contained traces of tyrosine, but a fourth was composed exclusively of cystine. This cystine possessed the same properties as that derived from the keratins.

J. C. D.

Hæmoquinic Acid. A New Disintegration Product of Quinine Present in the Urine, especially in "Blackwater" Fever. M. NIERENSTEIN (*J. Royal Army Med. Corps*, 1919, 215—217).—Occasionally, dark-coloured urines have been observed to follow the administration of quinine. These cases were examined for the presence of kynurenic acid, but without success. An extension of the method for the isolation of kynurenic acid led, however, to the isolation of a new disintegration product of quinine, *hæmoquinic acid*. The acid crystallised from dilute alcohol has m. p. 183° (decomp.). It may be recognised in dilutions as great as 1 in 5000 by means of the blue coloration given with Herapath's reagent. It yields a *picrate*, m. p. 224°, and a *sulphate* crystallising from water in small, silky needles. In addition to "blackwater" urines, the urines of the following malaria cases were also examined for this acid: (1) patients having quinine; (2) patients soon after rigor; (3) patients some time after rigor. The results of this study suggest a possible relationship between the formation of hæmoquinic acid in the organism and the production of "blackwater." Hæmoquinic acid shows pronounced hæmolytic properties towards human and sheep's corpuscles. It is possible that the acid is 6-methoxyquinoline-3-glyoxylic acid, $C_9NH_5Me \cdot CO \cdot CO_2H$.

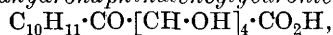
J. C. D.

Chitenine. A Disintegration Product of Quinine Found in the Urine. M. NIERENSTEIN (*J. Royal Army Med. Corps*, 1919, 218—219).—The observation of Kerner (*Arch. gesamt. Physiol.*, 1869, 200) that chitenine, an oxidation product of quinine, is found in the urine after the administration of quinine is confirmed. It is present in the urine in the early stages of the excretion of quinine. Chitenine was isolated from the urine of a normal individual collected during the first two or three hours after the administration of quinine sulphate by a fractionation of the precipitate produced on the addition of picric acid. The chitenine obtained from the urine crystallised from dilute alcohol in prisms, m. p. 281—282°, $[\alpha]_D^{25} - 122.6^\circ$, and showed other properties similar to those of the chitenine described by Skraup (A., 1893, i, 737).

J. C. D.

The Fate of Tetrahydronaphthalene (Tetralin) in the Animal Body. JULIUS POHL and MARGARETE RAWICZ (*Zeitsch. physiol. Chem.*, 1919, **104**, 95—104. Compare Schroeter and Thomas, A., 1918, i, 418).—Tetrahydronaphthalene is slightly

toxic, but rabbits weighing 2 kilos. can tolerate the administration of 2—3 grams by the stomach without showing apparent symptoms. Smaller animals develop diarrhœa and die, exhibiting narcosis. Tetrahydronaphthalene administered to the rabbit is excreted mainly as *ac-α-tetrahydronaphthaleneglycuronic acid*,



m. p. 256—258°, crystallising in colourless, lustrous plates. A small portion is excreted unchanged by the respiratory tract. When tetralin is administered orally to man, 5—7 grams per day, the urine is inactive, dark green, and readily yields an amorphous pigment. It also contains a leuco-compound, which is readily oxidised to a deep blue pigment, besides dihydronaphthalene and naphthalene. Dihydronaphthalene is chiefly excreted as the conjugated glycuronic acid, which readily yields naphthalene. Other substances isolated from the urines, such as *ac-α-tetrahydronaphthylcarbamide* and a substance melting at 286°, are regarded as products of secondary reactions.

J. C. D.

Chemistry of Vegetable Physiology and Agriculture.

Nitrate and Nitrite Assimilation. XIV. Iron and Oxygen as Necessary Agents for the Reduction of Alkali Nitrites by Auto-oxidisable Compounds. OSKAR BAUDISCH (*Ber.*, 1919, 52, [B], 35—40. Compare A., 1918, i, 474).—An explanation has now been found of the fact that iron as well as oxygen is necessary for the reduction. It has been shown (*loc. cit.*) that tervalent iron must be present in a complex form in order to produce nitric oxide or ammonia from an alkali nitrite. It is now shown that when an aqueous alkaline solution of sodium nitroprusside is boiled in the absence of air or oxygen, no nitric oxide is liberated, and that this gas is produced in large quantity directly oxygen is admitted to the system. A similar result is obtained by heating a solution of sodium carbonate and potassium nitrite with sodium ferripentacyanoammine, $[(CN)_5FeNH_3]Na_3$, in the presence of oxygen. The whole process of the reduction of alkali nitrite is, therefore, a replacement of inorganic or organic groups co-ordinatively attached to the iron atom by the NO-group of the alkali nitrite, and the subsequent elimination of this group by oxygen on warming. In accordance with this, nitrous acid is found in the distillate when a solution of potassium ferrocyanide is boiled with sodium carbonate and sodium nitrite in the presence of oxygen. The elimination of the cyano-group, however, occurs only very slowly, so that only slight traces of nitric oxide are formed, but this gas is liberated in considerable quantity when a little pyridine is added to the reaction mixture. The pyridine may be replaced by phloroglucinol.

Contrary to previous statements, it is not necessary that the compound capable of entering into complex salt formation with the iron must be auto-oxidisable in order to reduce alkali nitrites in alkaline solution by heating.

The reduction of alkali nitrite to nitric oxide and ammonia by an alkaline solution of dextrose containing an iron salt is now comprehensible in view of the formation of the complex iron salts which are produced with aldo- and keto-hexoses in alkaline solution. Oxanthrone behaves quite similarly to dextrose, and in both cases oxygen is unnecessary. C. S.

Nitrate and Nitrite Assimilation. XV. Iron and Oxygen as Necessary Agents for the Reduction of Alkali Nitrates.

OSKAR BAUDISCH (*Ber.*, 1919, **52**, [B], 40—43. Compare preceding abstract).—Experiments are recorded which show that an alkali nitrate is quite unaffected by boiling in alkaline solution with ferrous carbonate or hydroxide in the absence of oxygen, but is reduced through the alkali nitrite to ammonia directly oxygen is admitted. Alkali nitrite is reduced to ammonia even in the absence of oxygen.

The author invokes his peroxide formula of alkali nitrates (A., 1916, i, 702) to explain the phenomenon. Probably the oxygen and the ferrous hydroxide form a compound, $\begin{array}{c} \text{O} \\ \parallel \\ \text{O} \end{array} \text{Fe}(\text{OH})_2$, and this and the alkali nitrate, reacting together like two peroxides, produce oxygen and alkali nitrite; the latter is then reduced to ammonia. C. S.

Influence of Salts on the Nitric-Nitrogen Accumulation in the Soil.

J. E. GREAVES, E. G. CARTER, and H. C. GOLDTHORPE (*J. Agric. Res.*, 1919, **16**, 107—135).—The object of the investigation was to determine the relative toxicity and stimulant action of various salts applied to a soil, as measured by the effect on the nitrifying organisms. The salts tested were the chlorides, nitrates, sulphates, and carbonates of sodium, potassium, calcium, magnesium, manganese, and iron. It was found that the toxicity of these salts was determined by the specific nature of the salt, and not by the ions. In order of decreasing toxicity, the salts were: sodium sulphate, sodium carbonate, calcium carbonate, potassium sulphate, potassium carbonate, ferric nitrate, sodium nitrate, magnesium sulphate, ferric sulphate, calcium nitrate, potassium nitrate, potassium chloride, magnesium nitrate, manganous carbonate, manganous chloride, manganous sulphate, ferric carbonate, magnesium chloride, sodium chloride, calcium chloride, calcium sulphate. Increase of toxicity with concentration was much more rapid in some cases than in others. The explanation of the toxicity is probably physiological, due to the action of the salt on the living protoplasm of the bacterial cell, the increased osmotic pressure of the soil solution being subsidiary.

Most of the salts acted as stimulants to nitrification in some at least of the concentrations used. Those which failed to give any stimulation were sodium sulphate and carbonate, calcium carbonate, potassium sulphate and carbonate, and ferric nitrate. Many of the nitrates caused large losses of nitric nitrogen, due to conversion into protein nitrogen, and not to denitrification. The fixation of nitrogen was specially stimulated by the nitrates of magnesium, iron, calcium, and manganese. [See *J. Soc. Chem. Ind.*, 1919, 297A.] J. H. J.

Preparation of Glycerol by Fermentation. KARL SCHWEIZER (*Helv. Chim. Acta*, 1919, 2, 167—172).—Glyceraldehyde and dihydroxyacetone are commonly regarded as intermediate compounds in the conversion of sugar into alcohol. It is possible, therefore, that they are also the precursors of the glycerol which is formed during alcoholic fermentation, in which case it might be possible to increase the yield of glycerol if the process is carried out in the presence of a reducing agent. Owing to the sensitive nature of the ferment, the problem resolves itself into finding a hardy species of yeast and a reducing agent which does not hinder its development. A technical pressed yeast, prepared with molasses, and sodium sulphite were found to answer the requirements. On the experimental scale, the best result was obtained in a Hayduck apparatus with a mixture containing 40 grams of sucrose, 2 grams of ammonium dihydrogen phosphate, 1 gram of dipotassium hydrogen phosphate, and 10 grams of pressed yeast in 400 c.c. of water, to which 30 grams of sodium sulphite were added when the fermentation had started. After twenty-four hours, fermentation had stopped, and as a mean of several experiments 21.3 grams of glycerol were obtained from 100 grams of sucrose. As might be expected, less glycerol was formed if the mixture was thoroughly aerated.

It is stated that some of the belligerent nations have applied sodium sulphite in the manufacture of glycerol by fermentation on the large scale during the war. J. C. W.

Fumaric Acid Fermentation of Sugar. FELIX EHRLICH (*Ber.*, 1919, 52, [B], 63—64).—The formation of free fumaric acid during the fermentation of sugar by *Aspergillus fumarius* (Wehmer, this vol., i, 58) has been previously observed by the author during fermentation by *Rhizopus nigricans* (*Mucor stolonifer*) (A., 1912, ii, 192). C. S.

Determination of the Distribution of Nitrogen in Certain Seeds. J. F. BREWSTER and C. L. ALSBERG (*J. Biol. Chem.*, 1919, 37, 367—371).—Certain of the results have been reported previously (compare A., 1915, i, 760).—Yeast-nucleic acid, which was free from material giving a biuret reaction, was hydrolysed with 20% hydrochloric acid for twenty-five hours, and then analysed by the Van Slyke method for determining the distribution of

nitrogen in proteins. Fifteen % of the total nitrogen was found in the arginine fraction, although the nucleic acid contained no arginine. This indicates that in the determination of the distribution of nitrogen in materials containing nucleic acid by this method, erroneous results may be obtained, because purine and pyrimidine nitrogen may appear in the arginine fraction.

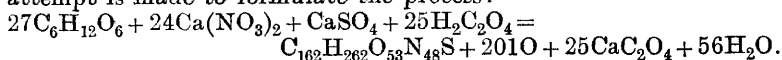
J. C. D.

The Influence of External Concentration on the Position of the Equilibrium Attained in the Intake of Salts by Plant Cells. WALTER STILES and FRANKLIN KIDD (*Proc. Roy. Soc.*, 1919, [B], 90, 448—470).—The authors have followed the course of intake of salts by carrot and potato tissue by measuring the changes in conductivity of the solution of a salt presented to the tissue, working with concentrations varying from $N/10$ to $N/5000$. Carrot tissue is much more suitable than potato tissue for work of this character, since the exosmosis from carrot into distilled water is slight, whilst that from potato is considerable. In the case of copper sulphate, exosmosis exceeds absorption at all concentrations, this being characteristic of toxic substances, and the initial rate of exosmosis increases with increase in concentration of the toxic solution. With aluminium sulphate, the curves showing the change in conductivity of the external solution were similar to those obtained with copper sulphate, although aluminium sulphate is not toxic. The authors suggest that this may be due to the absorption of the aluminium ion, its place being taken by hydrogen ions or some other ions, which results in an increase in the conductivity of the external solution.

Carrot tissue absorbs potassium, sodium, and calcium chlorides in all the concentrations examined, the absorption at first being approximately proportional to the external concentration. As the absorption progresses, however, it tends towards an equilibrium condition in which the ratio of internal to external concentration is not constant, but varies with the concentration. This ratio of final internal to final external concentration is called the absorption ratio, and may be expressed by the equation $y = kc^m$, where y is the final internal and c the final external concentration, k and m being constants. This is the adsorption equation, but the data given are regarded as inadequate to justify the conclusion that absorption of salts by the cell is an adsorption process. W. G.

Relationship between the Formation of Proteins and Acids in Leaves. ARTH. MEYER (*Ber. Deut. bot. Ges.*, 1918, 36, 508—513).—A review of the literature shows that slight protein formation accompanied by feeble deacidification and production of oxalate occurs in leaves kept in the dark; on exposure to light, the three processes occur to a greater extent. Protein and oxalate are readily formed in leaves exposed to light in an atmosphere free from carbon dioxide, and marked deacidification takes place simultaneously. The actions do not occur to more than a slight extent in the illuminated, colourless leaf.

The author is of the opinion that the carbohydrates react with nitrogen, sulphur, and phosphorus derived from inorganic salts to yield proteins; the bases of the salts are thereby liberated and neutralised by the organic acid produced in the leaves. An attempt is made to formulate the process:



Evidence in favour of such a scheme is deduced from the literature, and further quantitative data are promised. H. W.

Utilisation of Dextrose and Lævulose by Higher Plants.

H. COLIN (*Compt. rend.*, 1919, **168**, 697—699).—From an examination of etiolated leaves of beetroot, artichoke, and chicory fed by a root or a tubercle having a reserve of sucrose or inulin, the author produces further evidence in support of the view that lævulose is used by the cells more rapidly than is dextrose.

W. G.

Influence of certain Organic Compounds on the Development of Plants. III. G. CIAMICIAN and U. RAVENNA (*Atti R. Accad. Lincei*, 1919, [v], **28**, i, 13—20. Compare A., 1918, i, 473).

—The effect of watering bean plants grown on cotton wool with 0.1% solutions of various compounds related fundamentally to the vegetable alkaloids has been studied; the bases tested were applied in the form of tartrates or phosphates. Of the three methylamines, methylamine is the least toxic and the slowest, and trimethylamine the most toxic and the most rapid, in its action; small, yellowish-brown spots appear on the veins and then on the whole surface of the leaves, which finally dry up. The action exerted by tetramethyl- and tetraethyl-ammonium salts is less poisonous than, and different in its manifestation from, that of the amines. Theobromine and dimethylxanthine exert effects moderate in comparison with those of caffeine and trimethylxanthine. Methyluric acid has a distinctly toxic action, slow in appearing. Piperidine exerts a slight effect, but allows the plants to attain complete maturity, whereas 1-methylpiperidine, dimethylpiperidylammonium tartrate, conine, acetylpiperidine, and piperine are all more or less toxic. Unlike morphine, codeine and diacetylmorphine are markedly toxic. Cinchonine exhibits the same poisonous effects as quinine, but to a less degree. Atropine and cocaine are both toxic, the action of the latter being the more prompt and more intense. Papaverine and narcotine are somewhat more toxic than morphine and produce similar effects, and sparteine also has a poisonous action. Strychnine at first causes increased development of the plants, but these die later; nicotine also kills the plants, but in 0.01% solution is without effect. *iso*Amylamine rapidly produces fatal effects. Aniline is less poisonous than acetanilide, and this less so than methylacetanilide.

The above results indicate that introduction of methyl groups increases the toxicity of a compound, confirmation of this rule

being obtained with catechol and guaiacol. Potassium salicylate causes only retardation in development, whereas methyl salicylate exhibits distinct, although belated, toxicity.

Experiments with carbamide, guanidine, cyanamide, and potassium cyanate and cyanide show that cyanamide is the most poisonous of the first three compounds, and is followed by guanidine; carbamide, on the other hand, produces extraordinarily rank development of the plants. The cyanate and cyanide, both poisonous, determine retarded growth.

Some of the above poisonous compounds exert an influence on the migration of the starch, treatment of the leaves with iodine solution demonstrating the persistence of the starch at places where the action of light is excluded. The formation of starch also is sometimes retarded, coloration of the leaves by iodine exhibiting discontinuity in the form of spots and veinings.

T. H. P.

Microchemistry of Plants. XII. Large Siliceous Bodies in the Leaf of *Arundo Donax*. XIII. Behaviour of Cystolites towards Salts of Silver and other Metals.

HANS MOLISCH (*Ber. deut. Bot. Ges.*, 1918, **36**, 474—481. Compare this vol., i, 113).—Unusually large siliceous bodies, 72—108 μ long, 43—100 μ wide at the ends, and 11—54 μ wide at the middle, occur in the leaves of *Arundo Donax*; they are insoluble in all acids except hydrofluoric, and can readily be examined after treatment of the leaf with phenol.

All the cystolites which have been investigated possess the power of reducing silver nitrate or sulphate so strongly that they become blackened after a short period. This property can be conveniently utilised for the investigation of the distribution of cystolites in leaves, the effects being well marked even with small magnification. The deposition of silver is due to calcium carbonate, which encrusts the cystolites, and the action provides a confirmatory microchemical method for the detection of calcium carbonate in the plant. Cystolites become coloured red to bluish-violet in gold chloride solution, rust-red in ferrous sulphate, pale green in nickel sulphate, and lilac or pink in cobalt chloride or cobalt sulphate. The colorations are due to precipitates of the corresponding hydroxides caused by the calcium carbonate of the cystolites. H. W.

Production of Alcohol from Algæ. E. KAYSER (*Ann. Chim. anal.*, 1919, [ii], **1**, 79—80).—See this vol., i, 193.

Carbohydrate Content of Lichens and the Influence of Chlorides on Alcoholic Fermentation. E. SALKOWSKI (*Zeitsch. physiol. Chem.*, 1919, **104**, 105—128).—Analyses of Iceland moss (*Lichen islandicus*) and reindeer moss (*Cladonia rangiferina*) are given. The former contains 59.45% of lichenin, 4.3% of fat, 4.73% of protein, 19.47% of organic matter, exclusive of lichenin, 2.01% of ash, and 10.04% of water. The latter contains 54.63% of lichenin, 2.59% of ether extract, 4.1% of protein, 26.96% of other organic sub-

stances, 10.59% of water, and 1.13% of ash. Hydrolysis of these two lichens with 2.5% hydrochloric acid or 6% sulphuric acid yields 60—66% of the dry weight of the raw material as dextrose. The sugar is fermentable. Sodium chloride disturbs the fermentation of dextrose according to the amount present. The concentration of dextrose also has an influence. A 12% solution of dextrose containing 4% of sodium chloride is completely fermented, and nearly so when 8% of the salt is present. Only 90% of the sugar is fermented when a 20% solution containing 4% of sodium chloride is tested. The equivalent quantity of calcium chloride exerts a more disturbing influence. The hydrolysates from the lichens contain not only the readily fermentable sugar, but also a substance which inhibits fermentation. It is possible this property belongs to the acids from the lichens. Lichens contain a readily hydrolysable cellulose. Lichenin is not converted into sugar by the diastatic ferments of the pancreas or saliva or plant diastases. Iceland moss contains at least 10.92% of lichen acids calculated as cetraric acid, $C_{30}H_{30}O_{12}$.
J. C. D.

Application of the Biochemical Method to the Study of Several Species of Indigenous Orchids. Discovery of a New Glucoside, Loroglossin. EM. BOURQUELOT and M. BRIDEL (*Compt. rend.*, 1919, **168**, 701—703).—Using the method previously described (A., 1906, ii, 386), the authors have proved the presence in the aerial organ of a number of species of orchids of one or more glucosides hydrolysable by emulsin. From one of these orchids, *Loroglossum hircinum*, Rech., a new glucoside, *loroglossin*, has been isolated, having m. p. 137° (corr.), $[\alpha]_D -42.97^\circ$. It is hydrolysed by warm dilute sulphuric acid, as well as by emulsin. In addition, the plants contain sucrose and a considerable amount of a dextrorotatory substance, which is not attacked by ferments.
W. G.

The Flavones of Rhus. C. E. SANDS and H. H. BARTLETT (*Amer. J. Bot.*, 1918, **5**, 112—119; from *Physiol. Abstr.*, 1919, **3**, 578).—The wood flavone of *Rhus typhina* and *R. glabra* is fisetin, which is regarded as an end-product of metabolism. The distinctive leaf flavone of *R. glabra* and *R. copallina* is myricetin, which is probably a plastic substance. The authors agree with Perkin's views (T., 1896, **69**, 1299—1303, 1303—1309; 1898, **73**, 1016—1019; 1900, **77**, 423—432) that the flavones of the wood and of the leaves of *Rhus* are different.
W. G.

Chemical Investigations of some Poisonous Plants in the Natural Order Solanaceæ. III. Occurrence of Noryoscyamine in Solandra longiflora. J. M. PETRI (*Proc. Linn. Soc., N.S.W.*, 1917, **41**, 815—822; from *Physiol. Abstr.*, 1919, **3**, 581).—The leaves of *Solandra longiflora* contain alkaloids to the extent of 0.17% of the dry weight, the chief one being solandrone, and hyoscyamine is also present.
W. G.

Toxic Constituents in the Bark of *Robinia pseudacacia*, L. BUHACHIRO TASAKI and USHIO TANAKA (*J. Coll. Agric. Tokyo*, 1918, **3**, 337—356).—A new toxic glucoside, *robitin*, was isolated from the bark of *Robinia pseudacacia*. The air-dried bark was extracted with water, and the filtrate heated for half an hour at 80—90°, after which it was refiltered. The second filtrate was concentrated at 40° under reduced pressure to one-tenth of its volume. Impurities were separated by lead acetate, the excess of lead was then removed, and the process of concentration repeated. A reddish-brown extract was obtained, which was poured into absolute alcohol, when a white, flocculent precipitate was produced; this was washed with alcohol and dried in a vacuum. The yield was 3% of the dried bark. As thus prepared, robitin is a pure white, odourless, somewhat bitter, hygroscopic, amorphous powder, easily soluble in water and acids, but insoluble in organic solvents. It contained 3% of ash. On hydrolysis, it yielded glucose and rhamnose. [See *J. Soc. Chem. Ind.*, 1919, 267A.] J. H. J.

Copper and Zinc as Antagonistic Agents to the "Alkali" Salts in Soil. C. B. LIPMAN and W. F. GERICHKE (*Amer. J. Bot.*, 1918, **5**, 151—170; from *Physiol. Abstr.*, 1919, **3**, 586).—Pot cultures of barley were grown on soils containing sodium chloride, sulphate, and carbonate in toxic quantities, to which copper in the form of its sulphate, chloride, or carbonate, or zinc in the form of its chloride or sulphate, was added. It was found that the presence of copper or zinc brought about an increased yield. W. G.

Presence of Acetylmethylcarbinol in Saccharine Sorghum Silage. W. G. FRIEDEMANN and C. T. DOWELL (*J. Ind. Eng. Chem.*, 1919, **11**, 129—130).—Saccharine sorghum silage is found to contain a volatile compound which reduces Fehling's solution and is identified as acetylmethylcarbinol; the latter was previously shown to exist in cider vinegar. The fact that acetylmethylcarbinol yields acetic acid on oxidation renders untrustworthy the Duclaux method for estimating alcohols, since, according to this method, the proportion of ethyl alcohol is calculated on the basis of the amount of acetic acid formed on oxidation. The saccharine sorghum silage is the only one in which formic acid has been found, this observation being probably connected with the fact that acetylmethylcarbinol yields formic acid as one of its products of oxidation. In none of the other silages examined could the presence of volatile reducing compounds be detected. T. H. P.

The Atom of Bohr in Organic Chemistry. E. H. BUCHNER (*Chem. Weekblad*, 1919, **16**, 521—527).—A theoretical paper in which the author applies the ideas of Rutherford and Bohr regarding atomic and molecular structure to organic compounds. As a consequence of the assumed mode of atomic linking, the symmetrical tetrahedral structure of the methane molecule is deduced, the replacement of one or more hydrogen atoms by substituents causing deformation of the regular tetrahedron. The theory is further applied to the elucidation of the nature of the double bond between carbon atoms. This is shown to differ from the single bond only in the greater radius of the electron orbit, in which four electrons are present instead of two, and in the consequent increased distance between the carbon nuclei. The geometrical isomerism of maleic and fumaric acids, and the transformation of *cis*- into *trans*-forms, are discussed. Kekulé's representation of the benzene molecule as a uniplanar hexagon of alternate singly and doubly linked carbon atoms receives support from the theory. The possible existence of two isomeric ortho-disubstitution products of benzene is admitted, but, owing to the essential qualitative similarity of the single and the double bond, already referred to, it is pointed out that the difference in properties of two such isomerides would probably be imperceptible.

W. S. M.

A New Reaction of Paraffin Hydrocarbons. E. V. LYNN
(*J. Amer. Chem. Soc.*, 1919, **41**, 368—370).—When the reddish-brown solution of nitrosyl chloride in *n*-heptane is exposed to sun-
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light, it gradually becomes blue and deposits ammonium chloride. The blue colour soon fades, and the turbid liquid then deposits a yellow oil, considerable volumes of hydrogen chloride being evolved. The oil decomposes further when submitted to steam distillation, hydroxylamine remaining in the residue. The distillate is very fragrant, and apparently consists of a mixture of the three *n*-heptanones, although no fraction yielded the *semicarbazone* of dipropyl ketone, m. p. 125°, which was made from calcium butyrate for comparison. Light petroleum exhibits the same phenomena.

In the case of heptane, it is assumed that the main reactions may be represented thus: $C_7H_{16} + NOCl = HCl + C_7H_{15}\cdot NO$ (blue), $C_7H_{15}\cdot ON \rightarrow C_7H_{14}\cdot N\cdot OH$ (oil), and this $+ H_2O = C_7H_{14}O + NH_2\cdot OH$.
J. C. W.

Ethylene. WILLIAM MALISOFF and GUSTAV EGLOFF (*J. Physical Chem.*, 1919, **23**, 65—138).—A résumé of the present state of knowledge of the physical and chemical properties of ethylene, and of the processes of its formation and decomposition. A very full bibliography is given.
W. G.

The Action of Monosodioacetylene on some Halogen Esters of Secondary and Tertiary Alcohols. PICON (*Compt. rend.*, 1919, **168**, 825—828).—The primary alkyl haloids react with monosodioacetylene in liquid ammonia to give homologues of acetylene (compare A., 1913, i, 438; 1914, i, 647). The secondary and tertiary alkyl haloids under similar conditions do not, however, give acetylenic hydrocarbons, but ethylenic hydrocarbons, a molecule of the hydrogen haloid being eliminated; thus:



W. G.

Action of Monosodioacetylene on some Iodides of Primary Alcohols with Branched Chains. PICON (*Compt. rend.*, 1919, **168**, 894—896. Compare preceding abstract).—*iso*Butyl iodide when acted on by monosodioacetylene in liquid ammonia in an autoclave at the ordinary temperature is decomposed, giving *isobutylene*. Commercial *iso*amyl iodide, which is a mixture of the inactive and active forms, under similar conditions yields *isoheptinene* and β -methyl- Δ^a -butene, together with a condensation product. The *isoheptinene* and the condensation product come entirely from the *i-iso*amyl iodide, whilst the *iso*amylenes come from the active isomeride.

Alkyl iodides of the type $R\cdot CH_2\cdot CH_2I$ yield true acetylenic hydrocarbons when decomposed by monosodioacetylene, whereas from iodides of the types $R\cdot CHR'\cdot CH_2I$ or $R\cdot CH_2\cdot CHR'I$ an ethylenic hydrocarbon is always formed. This formation of an ethylenic hydrocarbon is shown not to be due to the presence of traces of water or to any action of the liquid ammonia on the alkyl iodide.
W. G.

Action of Magnesium Phenyl Bromide on Polyhalogenated Derivatives of Ethane. FRED. SWARTS (*Bull. Soc. chim.*, 1919, [iv], 25, 145—174).—In an endeavour to prepare difluorobromoethylbenzene by the action of magnesium phenyl bromide on $\alpha\alpha$ -difluoro- $\alpha\beta$ -dibromoethane, the author could only obtain difluoroethylene. He then studied this reaction with a number of other polyhalogenated derivatives of ethane, using, in every case, one molecule of the organomagnesium compound and one molecule of the substituted ethane. The reaction was, in every case, complex and gave rise to several different compounds. In the case of the bromo-derivatives of ethane, the principal reaction consisted in the elimination of two halogen atoms and the formation of an ethylene derivative and bromobenzene. When the halogenated ethane had an atom of fluorine and an atom of bromine attached to the same carbon atom, it was always the atom of bromine which was eliminated. In the case of a compound of the type $\text{CH}_2\text{I}\cdot\text{CHF}_2$, where an atom of fluorine and an atom of iodine were eliminated, the principal reaction always proceeded according to the equation $\text{CH}_2\text{I}\cdot\text{CHF}_2 + \text{MgPhBr} = \text{CH}_2\text{:CHF} + \text{PhI} + \text{MgBrF}$. The chloro-derivatives behaved differently from the fluoro-, bromo-, or iodo-derivatives of ethane in that, instead of two halogen atoms being eliminated, a molecule of hydrogen haloid was eliminated. Thus tetrachloroethane yielded trichloroethylene and $\beta\beta$ -difluoro- $\alpha\alpha$ -dichloroethane yielded fluorodichloroethylene.

In several of the reactions where magnesium fluoride was formed, this salt was obtained in the form of a colloidal solution in water, the salt not being immediately precipitated by the addition of acid, and in certain cases the magnesium fluoride remained dissolved in ether.

In addition to the above general reaction, a number of secondary actions occurred, of which the most constant was the formation of diphenyl. The formation of this compound is most marked where the general reaction is slow, and less noticeable when the reaction is violent.

W. G.

Action of Alkaline Reducing Agents on Iodoform. A. GUTMANN (*Ber.*, 1919, 52, [B], 212—215).—When iodoform is added to a solution of arsenious oxide in about 27% sodium hydroxide, reaction takes place almost quantitatively, according to the equation $\text{CHI}_3 + \text{Na}_3\text{AsO}_3 + \text{NaOH} = \text{CH}_2\text{I}_2 + \text{NaI} + \text{Na}_3\text{AsO}_4$. Iodoform also oxidises sodium antimonite and stannite, and an alcoholic solution liberates sulphur from fresh sodium sulphide. When warmed with a mixture of sodium sulphide and cyanide, it produces a thiocyanate, but it will not oxidise a sulphite. J. C. W.

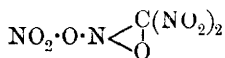
Preparation of Tetranitromethane. KENNEDY JOSEPH PREVITÉ ORTON (*Brit. Pat.*, 125000).—Acetylene is passed into nitric acid of 90—97·5% strength, preferably at a temperature of about 40°; absorption occurs more readily in the presence of mercury or a mercury salt, whereby also the yield is improved

when the operation is performed at 40°, but not at lower temperatures. The product is now mixed with sulphuric or fuming sulphuric acid under conditions excluding rise in temperature, and the mixture is gradually heated until the tetranitromethane distils, or slowly heated in a reflux apparatus until gas ceases to be evolved and then distilled. Apparently, the chief product of the action of acetylene on nitric acid is an intermediate compound, which is converted into tetranitromethane when the solution is heated with sulphuric acid. [See also *J. Soc. Chem. Ind.*, 1919, June.]

H. W.

Constitution of Tetranitromethane. ERICH SCHMIDT (*Ber.*, 1919, 52, [B], 400—413).—From the results of a quantitative study of the behaviour of tetranitromethane towards aqueous potassium hydroxide, it appears that the substance is decomposed in two ways, according to the equations: (1) $\text{C}(\text{NO}_2)_4 + 2\text{KOH} = \text{KNO}_3 + \text{KC}(\text{NO}_2)_3 + \text{H}_2\text{O}$ (compare Hantzsch and Rinkenberger, *A.*, 1899, i, 404), and (2) $\text{C}(\text{NO}_2)_4 + 6\text{KOH} = 4\text{KNO}_2 + \text{K}_2\text{CO}_3 + 3\text{H}_2\text{O}$. The course of the reaction depends on the concentration of the alkali; the ratio of the quantity reacting according to the first equation to that according to the second varies from 2:1 with 0.1*N*-alkali to 12:1 with 14*N*-alkali.

Iodotritnitromethane only reacts in one direction, however, analogous to (1) above: $3\text{CI}(\text{NO}_2)_3 + 6\text{KOH} = 3\text{KC}(\text{NO}_2)_3 + 2\text{KI} + \text{KIO}_3 + 3\text{H}_2\text{O}$ (Hantzsch, *A.*, 1906, i, 617). The dual nature of tetranitromethane is therefore connected with the fourth "nitro"-group, and the facts can be explained on the assumption that the compound exists in the tautomeric forms



(Willstätter and Hottenroth, *A.*, 1904, i, 472) and $\text{NO} \cdot \text{O} \cdot \text{C}(\text{NO}_2)_3$. The first form reacts according to equation (1), and is favoured by concentrated alkalis, whilst the second isomeride reacts according to equation (2).

In the quantitative study of the reaction, the following estimations were made: (1) The alkali required in the case of the 0.1*N*-solution. Sealed bulbs of the nitro-compound were crushed under the potassium hydroxide, and the excess of alkali was titrated, using phenolphthalein. (2) The nitrite. Immediately after the reaction with the alkali was completed, the clear solution was neutralised in the cold, and the nitrite estimated as nitrogen by means of ammonium chloride. (3) The carbonate. Some reactions were performed with 0.1*N*-barium hydroxide, and the barium carbonate produced was converted into the sulphate and weighed. (4) The nitrate. The product of the reaction with 0.1*N*-alkali was mixed with palladinised barium sulphate and concentrated potassium hydroxide, and treated with hydrogen until the solution became pale yellow. The nitroform was thereby reduced to an unknown compound, but the nitrate left almost untouched. The

filtered solution was then evaporated, dropped on hydrazine sulphate to decompose the nitrite, diluted, filtered again, acidified with sulphuric acid, and precipitated with nitron acetate. (The preparation of palladinised barium sulphate is described.) (5) The nitroform. The nitrite was decomposed by boiling with ammonium chloride, and then the solution was transferred to a flask with a ground-in still-head, acidified with phosphoric acid, and boiled until the nitroform had passed over, this being trapped in 0.1*N*-potassium hydroxide. The solution was acidified with acetic acid and precipitated with nitron acetate.

Tetranitromethane also decomposes into a nitrite when treated with dilute hydrochloric acid, for dimethyl-*m*-toluidine can be converted into its *p*-nitroso-compound by such a mixture.

The following salts of nitroform have been prepared: the stable *nitron* salt, $C_{20}H_{16}N_4 \cdot CH(NO_2)_3$, decomp. 136—141°; *di-isobutylamine* salt, decomp. 121—123°; *piperidine* salt, notched leaflets, decomp. 100°; *dibenzylamine* salt, needles, decomp. 160—163°.

J. C. W.

Preparation of Optically Active Propylene Glycol. AD. GRÜN (*Ber.*, 1919, **52**, [B], 260—263).—Abderhalden has recently isolated the active forms of propylene glycol (this vol., i, 2), but Grün had already studied the subject with the partial success now described.

Propylene glycol is left with concentrated sulphuric acid at the ordinary temperature, and the inactive *dihydrogen disulphate*, $C_3H_6(O \cdot SO_3H)_2$, is isolated as the *barium* salt, $3H_2O$, which is converted into the *potassium* salt, leaflets, 0.5EtOH, *sodium* salt, needles, and *strychnine* salt. Two modifications of the last salt are obtained: pearly tablets, $[\alpha]_D^{20} - 20.38^\circ$, of which 0.9 gram dissolves in 100 c.c. of water, and rosettes of long, slender needles, $[\alpha]_D^{20} - 28.19^\circ$, with the solubility 11.82. By treatment with 0.2*N*-barium hydroxide, the tablets have been converted into the *barium* salt of *d-propylene dihydrogen disulphate*, $[\alpha]_D^{20} + 11.50^\circ$, but further progress in the isolation of *d*-propylene glycol could not be made, owing to the great stability of the free acid ester.

J. C. W.

Some Derivatives of Trimethylene Glycol. ERICH SCHMIDT and RUDOLF WILKENDORF (*Ber.*, 1919, **52**, [B], 389—399).—Henry found in 1895 that “nitroisobutylglycerol,” $NO_2 \cdot C(CH_2 \cdot OH)_3$, could be obtained readily by the condensation of nitromethane with formaldehyde under the influence of alkali hydroxides, but all his attempts at controlling the reaction so as to give nitrotrimethylene glycol were unsuccessful. The present authors have also found that partial condensation is hopeless, but have succeeded in making the glycol by the action of sodium methoxide solution on the glycerol, one molecule of formaldehyde being eliminated.

Nitroisobutylglycerol [nitrotrihydroxymethylmethane] is produced in 79% yield by warming a solution of nitromethane and

paraformaldehyde in dry ethyl acetate with a few drops of 33% potassium hydroxide. This is an improvement on Henry's method (A., 1896, i, 4). The *tribenzoate*, $\text{NO}_2 \cdot \text{C}(\text{CH}_2 \cdot \text{OBz})_3$, obtained by the action of benzoyl chloride and quinoline, crystallises in needles, m. p. 111° . The trihydric alcohol may also be prepared in methyl-alcoholic solution, and if such a solution is chilled and slowly mixed with sodium methoxide solution, *sodionitrotrimethylene glycol*, $\text{NO}_2 \cdot \text{CNa}(\text{CH}_2 \cdot \text{OH})_3$, separates in small prisms with 2MeOH , which crystallise with $2\text{H}_2\text{O}$ from aqueous alcohol, the yield being 91%. The salt decomposes vigorously at 130 — 136° , and gives the red colour with ferric chloride and the blue with ethereal hydrogen chloride, characteristic of the salts of nitro-paraffins. The salt is converted into free *nitrotrimethylene glycol* by boiling with ethereal salicylic acid. The compound crystallises from a mixture of ethyl acetate and chloroform in groups of feathery needles, m. p. 56 — 58° , is soluble in oxygenated solvents, does not give a colour with ferric chloride, is neutral to litmus, reduces ammoniacal silver oxide, decomposes when treated with benzoyl chloride and quinoline, and condenses with formaldehyde to give the above nitro*iso*-butylglycerol.

If the sodium salt is treated with ethereal bromine, it gives a 97% yield of *bromonitrotrimethylene glycol*, which crystallises in groups of stout prisms, m. p. 120 — 122° , and forms a *dibenzoate*, $\text{NO}_2 \cdot \text{CBr}(\text{CH}_2 \cdot \text{OBz})_3$, in highly refractive prisms, m. p. 104° .

The nitro-compound is reduced by means of hydrogen, catalysed by palladinised barium sulphate, in oxalic acid solution. *Amino-trimethylene glycol* is a strongly alkaline syrup with a bitter taste, and forms a snow-white *oxalate*, decomp. 202° . When benzoylated by the Schotten-Baumann method, it yields the *N-benzoyl* derivative, which crystallises in delicate needles, m. p. 131° , with a bitter taste, whereas in the presence of quinoline the *tribenzoyl* derivative, $\text{NHBz} \cdot \text{CH}(\text{CH}_2 \cdot \text{OBz})_3$, is formed. This crystallises in needles, m. p. 136° , which no longer taste bitter. J. C. W.

Dichloroethyl Sulphide (Mustard Gas). III. Solubility and Hydrolysis of Dichloroethyl Sulphide with a New Method for Estimating Small Amounts of the Same. E. F. HOPKINS (*J. Pharm. Expt. Ther.*, 1919, 12, 393—403).—The solubility of dichloroethyl sulphide in water has been determined, and at 10° has been found to be approximately 0.07%. The velocity of hydrolysis of dichloroethyl sulphide has been measured at 0.6° , 10° , 20° , 30° , and 37.5° ; the data are graphically represented in a series of curves. The hydrolysis is found to follow the equation for a unimolecular reaction.

Dichloroethyl sulphide in admixture with air may be rapidly estimated by bubbling the gas through a series of two tubes containing water at 35° ; the gas is rapidly absorbed and hydrolysed, and the hydrogen-ion concentration of the solution is then measured, methyl-red being used as indicator. It is necessary that all the glassware used should be insoluble in water. H. W.

Mercury Mercaptide Nitrites and their Reaction with the Alkyl Iodides. VI. Chain Compounds of Sulphur (*continued*).
SIR PRAFULLA CHANDRA RÂY (T., 1919, 114, 548—552).

Preparation and Hydrolysis of Esters Derived from the Substituted Aliphatic Alcohols. GEORGE R. BANCROFT (*J. Amer. Chem. Soc.*, 1919, 41, 424—431. Compare A., 1918, i, 2).—A study of the rate of hydrolysis by 0.1*N*-hydrochloric acid of the acetates of β -chloroisopropyl, $\beta\beta'$ -dichloroisopropyl, $\beta\gamma$ -dichloro- and $\beta\gamma$ -dibromo-propyl alcohols. As in the case of β -substituted ethyl acetates, it is found that the presence of a halogen atom in the β -position retards hydrolysis, the influence being still more pronounced in the case of $\beta\gamma$ -disubstituted esters, but most striking in the case of esters with two halogens in the β - and β' -positions.

The esters were obtained as follows: $\beta\beta'$ -dichloroisopropyl acetate, b. p. 201—203°, by the action of acetyl chloride on $\beta\beta'$ -dichlorohydrin; $\beta\gamma$ -dichloropropyl acetate, b. p. 197—198°, in a similar manner, the alcohol being formed by chlorinating allyl alcohol; β -chloroisopropyl acetate, b. p. 149—150°, in the same way, the alcohol being obtained by adding concentrated sulphuric acid to allyl chloride at 0°, and then, after keeping a day, diluting with water and boiling, thus: $\text{CH}_2\text{:CH}\cdot\text{CH}_2\text{Cl} + \text{H}_2\text{SO}_4 \rightarrow \text{CH}_2\text{Cl}\cdot\text{CHMe}\cdot\text{SO}_3\cdot\text{OH} \xrightarrow{\text{H}_2\text{O}} \text{OH}\cdot\text{CHMe}\cdot\text{CH}_2\text{Cl} + \text{H}_2\text{SO}_4$; the alcohol is isolated by distilling the solution (up to 130°), neutralising the distillate with potassium carbonate, saturating with salt, and extracting with ether.

In the preparation of allyl chloride by the action of phosphorus trichloride on allyl alcohol, advantage may be taken of the insolubility of the chloride in water to separate it from the phosphorous acid.
J. C. W.

Preparation of *iso*Butyl Oleate. ERNST PREISWERK (Brit. Pat., 123685).—*iso*Butyl oleate, prepared by condensing oleic acid or its chloride with *isobutyl* alcohol by the usual methods, has b. p. 190°/4 mm. and D_{20}^{20} 0.86. It is insoluble in water and possesses healing properties in cases of tuberculosis.

Hydrolysis of Glycollide and Lactide in Acid Solution. HJALMAR JOHANSSON and HUGO SEBELIUS (*Ber.*, 1919, 52, [B], 745—752).—Glycollide and lactide are hydrolysed by water to glycollic and lactic acids with intermediate formation of glycollo-glycollic and lacto-lactic acids respectively: $\text{O} \begin{smallmatrix} \text{CO}\cdot\text{CH}_2 \\ \text{CH}_2\cdot\text{CO} \end{smallmatrix} \text{O} + \text{H}_2\text{O} = \text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OH}$; $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OH} + \text{H}_2\text{O} = 2\text{OH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$. The authors have particularly investigated the first phase of the reaction, since the second is known to proceed normally. It occurs too rapidly in alkaline solution to permit accurate measurement. In moderately acid solution, the change takes the form of two independent, simultaneous reactions, only one of which is catalysed by hydrogen ions.

It therefore appears that hydrolytic fission of β -lactones is catalysed slightly or not at all by hydrogen ions, that of γ -lactones is catalysed, whilst the opening of the six-membered ring of glycolide or lactide proceeds either with or without catalytic assistance of hydrogen ions.

The experiments were carried out by adding solutions of glycolide or lactide in anhydrous acetone to water or dilute acid at $19.8 \pm 0.1^\circ$; at suitable intervals, aliquot portions of the solution were added to a solution of potassium iodide and potassium iodate, and the liberated iodine was estimated by titration with sodium thiosulphate after allowing sufficient interval for the complete liberation of iodine. The results are probably slightly low, the error, however, not exceeding 1%. The presence of acetone does not affect the titration, whilst the secondary hydrolysis of the ester acid occurs so slowly that it need not be taken into account.

H. W.

The Basic Properties of Oxygen in Organic Acids and Phenols; and the Quadrivalency of Oxygen. JOSEPH KNOX and MARION BROCK RICHARDS (T., 1919, 114, 508—531).

Pasteur's Principle of the Relation between Molecular and Physical Asymmetry. VIII. On the Spontaneous Fission of Racemic Potassium-Cobalti-oxalate into its Optically Active Antipodes. F. M. JAEGER and WILLIAM THOMAS (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, 21, 693—706).—When an aqueous solution of inactive potassium cobalti-oxalate is allowed to crystallise at temperatures near 0° , the racemic salt separates in the form of dark green, almost black triclinic pinacoidal crystals of the composition $K_3\{Cr(C_2O_4)_3\}3\frac{1}{2}H_2O$, D_4^{15} 1.877. These crystals are not isomorphous with those of the corresponding triclinic chromium, rhodium, and iridium salts; the water content being different (A., 1918, i, 3). When, however, the inactive solution is allowed to crystallise near 18° , separate crystals of the *d*- and *l*-compounds are deposited. These have trigonal trapezohedral symmetry, and are isomorphous with the corresponding optically active rhodium and iridium salts: $a:c=1.0:8968$, α $100^\circ 27'$, D_4^{15} 1.8893. Only on rare occasions could the *d*- and *l*-crystals be distinguished by the presence of hemihedral faces, in spite of their enormous optical activity. This is the first fully substantiated example of the spontaneous fission into its components of such a racemic complex metallic compound. The transition temperature of the racemic compound into its components, determined by the solubility method, was found at 13.2° .

The dark green solution of the active salt shows a pronounced absorption band between 5510 and 6520 Å.U. The form of the rotatory dispersion curve is noteworthy. The molecular rotation increases rapidly with increasing wave-length, but in the vicinity of the absorption band falls steeply, assuming the opposite algebraic sign at about 6260 Å.U., and reaching a maximum in the other

direction at about 6400 Å.U. The curve is similar in type to that of potassium chromium oxalate, the latter, however, showing a much greater absolute rotation on either side of the zero line. The positions of the maxima and minima are also different in the two salts, corresponding with the different positions of the absorption bands. For certain wave-lengths, the two *d*-forms (or *l*-forms) actually have opposite rotations. The influence of the specific nature of the central metallic atom is shown in the fact that the potassium rhodium- and iridium-oxalates have normal rotatory dispersion curves. E. H. R.

The Supposed Diastatic Properties of Formaldehyde. HERMANN SALLINGER (*Ber.*, 1919, 52, [B], 651—656).—A further contribution to the controversy on this subject (compare Woker, A., 1917, i, 61, 447; Kaufmann, A., 1917, i, 251). The author considers that the only valid evidence of the enzymatic indifference of formaldehyde towards starch is obtained by observation of the specific rotation and absence of reducing power towards Fehling's solution which can be ascribed to the action of formaldehyde on starch. With regard to the first point, a solution of amylopectin (Lintner) is found to retain its optical activity unchanged after digestion with formaldehyde during forty-four hours at 37°, thus confirming Kaufmann's previous observation. With regard to the second point, a solution of soluble starch (Wolff, Fernbach), after treatment with formaldehyde and removal of the latter as completely as possible, only showed slight reducing power towards Fehling's solution, which depended on traces of residual formaldehyde. Further, in a comparative series of experiments in which formaldehyde solutions of differing concentration were mixed on the one hand with starch solution and on the other with water, and subsequently treated with Fehling's solution, a greater reduction was not found in any instance in the solutions containing starch than in those from which it was absent. The author therefore considers formaldehyde to be enzymatically indifferent to starch. H. W.

The Relations between the Chemical Structures of Carbonyl Derivatives and their Reactivities toward Salts of Semicarbazide. ARTHUR MICHAEL (*J. Amer. Chem. Soc.*, 1919, 41, 393—424).—The velocities of the reactions of aldehydes and ketones with various reagents have been investigated quantitatively, chiefly by Petrenko-Kritschenko, and the results discussed in their theoretical aspects (see Stewart, "Stereochemistry," 474—501). The velocity factor in such reactions depends mainly on the magnitude of the free chemical energy of the carbonyl group and on its affinity relationships to the component parts of the reagent. From a determination of the reaction velocities of different ketones towards the same agent, conclusions may be drawn as to the influence of structure on the free energy of the carbonyl group, but this is not necessarily the same as discussing the reactivity of the

ketone. Reactivity is frequently confused with instability, but the latter term should be restricted to the behaviour of a compound towards physical forces, and the former used only in reference to the behaviour of a certain atom or group of atoms in a given chemical system. The reactivity of a ketone, for example, is the sum total of the changes in the free and bound chemical energy in all the atoms, manifesting itself at the carbonyl group because the hindrance to chemical change is best overcome at this point.

The present investigation has for its chief aim the arrangement of groups of carbonyl derivatives according to the relative reactivities of the members towards certain reagents. For such a purpose, semicarbazide is the most suitable agent, since its salts are only slightly hydrolysed in solution and most semicarbazones are only sparingly soluble in water. As a preliminary to the formation of a semicarbazone from a salt of semicarbazide, a carbonyl derivative must liberate the base, that is, it must exert as much energy as was dissipated in the neutralisation of the base by the acid. Since semicarbazide is a strong base, this energy will stand in direct relation to the affinity constant of the acid. The reactivity of a carbonyl compound can therefore be gauged by finding at what limit it ceases to react with a series of semicarbazide salts. Some carbonyl derivatives react with salts of semicarbazide and the strongest mineral acids. In such cases, the limit is ascertained by adding some of the free acid and finding how much is necessary to prevent reaction, or, in other words, to make the reverse hydrolysis of the semicarbazone to proceed with equal velocity. A similar method is employed in the case of two carbonyl derivatives which both react with the semicarbazide salt of one acid, but not with the salt of the next stronger acid; the more reactive compound is the one which forms a semicarbazone in the presence of the greater amount of the free acid.

Semicarbazide, m. p. 95° , and the following salts were employed in the experiments: hydrochloride, m. p. 175° ; hydrogen sulphate, m. p. 145° (decomp.); sulphate, m. p. 143° ; formate, m. p. 126° ; benzenesulphonate, plates, m. p. 187° (decomp.); acetate, m. p. 75° ; chloroacetate, m. p. $111-112^{\circ}$; dichloroacetate, m. p. 108° ; trichloroacetate, m. p. 154° (decomp.); oxalate, m. p. 133° (decomp.); maleate, m. p. 100° ; hydrofluoride; salicylate, m. p. 153° ; *o*-nitrobenzoate, m. p. 96° .

These salts and mixtures of them with the free acids fall into the following order when the difficulty of a ketone to liberate and react with the base is considered: (1) free base; (2) acetate; (3) formate; (4) chloroacetate; (5) oxalate; (6) dichloroacetate; (7) dichloroacetate + $0.5N$ -acid; (8) trichloroacetate; (9) hydrochloride; (10) hydrochloride + $0.2N$ -HCl; (12) hydrochloride + $0.5N$ -HCl; (13) hydrochloride + $0.6N$ -HCl; (15) hydrochloride + $1.0N$ -HCl. This order, therefore, may be regarded as the scale of reactivity.

In the first series of experiments, the reactions between aliphatic ketones and these agents in aqueous solution are described. For

the purpose, 0.5 mg.-mol. of the ketone was shaken with 0.8 c.c. of a solution containing 0.56 mg.-mol. of the salt, and any precipitates were purified and examined. No experiment was considered negative under 200 hours. The origins of the ketones are summarised, and the results are described in detail, discussed at some length, and reproduced by curves, particular attention being paid to the influence of branched chains. The least reactive ketone is propyl isopropyl ketone (1 on the scale), and the most reactive are methyl hexyl (12) and methyl octyl ketones (15). Dimethyl, diethyl, and dipropyl ketones come about 6 on the scale.

In a second series of experiments, alcoholic media were employed, 0.5 mg.-mol. of the ketone in 0.85 c.c. of alcohol of D 0.9270, or 0.9097 for the highest members, was shaken with 0.5 mg.-mol. of the reagent in the same volume of the same alcohol, and then at different intervals up to five months a few drops of the solution were evaporated and tested for a semicarbazone. Under such conditions, practically all the ketones only react with the free base; only the higher members, such as methyl hexyl ketone (10), show any great reactivity. The insolubility of the semicarbazone is obviously of considerable importance, but even in these cases in which the mixture remains homogeneous there is no connexion between reactivity and reaction velocity. Methyl hexyl ketone, for example, has the largest reactivity with semicarbazide in alcohol, but the velocity of its reaction with phenylhydrazine is only about half, and its velocity with potassium hydrogen sulphite about one-quarter, of the acetone velocities.

Acetophenone takes the ninth place on the scale and propiophenone about the fourth.

With the aldehydes, the outstanding feature is the great reactivity of formaldehyde and the aromatic aldehydes. These all react with semicarbazide hydrochloride even in the presence of 10*N*-hydrochloric acid. The changes from $\text{H}\cdot\text{CHO}$ to $\text{Me}\cdot\text{CHO}$ and $\text{C}_6\text{H}_5\cdot\text{CHO}$ to $\text{C}_6\text{H}_5\cdot\text{COMe}$ are accompanied by great falls in reactivity.

Several ketonic esters have also been investigated. Ethyl acetoacetate is much more reactive than the alkylacetoacetates, $\text{COMe}\cdot\text{CHR}\cdot\text{CO}_2\text{Et}$ and $\text{COMe}\cdot\text{CR}_2\cdot\text{CO}_2\text{Et}$, and is more reactive than ethyl benzoylacetate.

The following appear to be new: *methyl octyl ketone semicarbazone*, m. p. 119° ; *ethyl methylacetoacetate semicarbazone*, pale blue crystals, m. p. $183\text{--}187^\circ$ (decomp.); *ethyl ethylacetoacetate semicarbazone*, m. p. 154° (decomp.); *ethyl dimethylacetoacetate semicarbazone*, m. p. $183\text{--}187^\circ$ (decomp.); *ethyl allylacetoacetate semicarbazone*, m. p. 125° ; *ethyl diacetylmalonate semicarbazone*, $\text{C}_{13}\text{H}_{25}\text{O}_6\text{N}_6$; *ethyl oxaloacetate semicarbazone*, m. p. 162° ; *ethyl benzoylacetate semicarbazone*, m. p. 125° (decomp.).

Some practical applications of the above classification of the ketones may be mentioned. In the first place, a scheme for the separation of a mixture of ketones could be designed, based on the treatment of the mixture with solutions of semicarbazide salts in

decreasing order of the strengths of the acids. Secondly, strong acids may be classified according to their reactivities in concentrated solutions by finding what excess of acid is necessary to inhibit the formation of the semicarbazone of a suitable ketone.

J. C. W.

Mutarotation of Dextrose and Lævulose. J. M. NELSON and FRANK M. BEEGLE (*J. Amer. Chem. Soc.*, 1919, **41**, 559—575).—The specific rotation of α -*D*-glucose, β -*D*-glucose, and β -*D*-fructose has been determined at 0.15°, 15°, 25°, and 37°. The values found are: α -*D*-glucose, +111.2°; β -*D*-glucose, +17.5°; and β -*D*-fructose, -130.8°. These values are constant for all the temperatures investigated. The relation between the rate of mutarotation of the three sugars and varying concentrations of hydrogen ion has been determined. It is shown that the equilibrium rotation of dextrose is not affected by temperature, whilst that of lævulose varies with the temperature of the solution. The mutarotation of dextrose appears to be simply racemisation, whilst that of lævulose is not. The mutarotation of dextrose and lævulose in the presence of each other and in the presence of sucrose and invertase has been measured, and in each case was found to be independent of the other when present, except in the case of solutions of lævulose and sucrose, when the rate of mutarotation and the rotation at equilibrium were affected. The temperature-coefficient of the mutarotation was also determined.

J. F. S.

Glycollonitrile-*D*-glucoside, $C_6H_{11}O_5 \cdot O \cdot CH_2 \cdot CN$. EMIL FISCHER (*Ber.*, 1919, **52**, [B], 197—200. Compare A., 1917, i, 658).—The isolation of *glycollonitrile-D-glucoside* by the hydrolysis of its tetra-acetyl derivative with methyl-alcoholic ammonia is now described. It is an amorphous substance, $[\alpha]_D^{19} - 45.97^\circ$, which is soluble in cold water or pyridine, but not in most indifferent organic media, and it is very susceptible to hydrolytic influences. It is not so readily affected by emulsin, however, as mandelonitrile glucoside is, the best conditions being when the *H*-ion concentration is about $10^{-5.2}$. Hydrogen cyanide is formed during the hydrolysis. Proof of the purity and identity of the compound lies chiefly in its re-acetylation to tetra-acetylglucosidoglycollonitrile.

J. C. W.

Syntheses of Linamarin and Glycollonitrile Celloside. EMIL FISCHER and GERDA ANGER (*Ber.*, 1919, **52**, [B], 854—868).—The synthesis of linamarin, effected on lines similar to those followed by Fischer and Bergmann (A., 1917, i, 657) in the syntheses of mandelonitrile glucoside and sambunigrin, has already been described (A., 1918, i, 526).

Ethyl tetra-acetylglucosido- α -hydroxyisobutyrate is converted by aqueous barium hydroxide into *glucosido- α -hydroxyisobutyric acid*, prisms, m. p. 146—147° (corr.), $[\alpha]_D^{20} - 23.06^\circ$ in water. The physical constants of the synthetic linamarin differ slightly from those recorded for the natural substance, particularly in respect

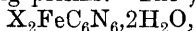
to optical activity, but the differences are not sufficiently great to cause any doubt as to the identity of the products. Both the synthetic and natural glucosides are slowly hydrolysed by emulsin, more rapidly by phaseolunataase from *Phaseolus lunatus*. The substance is in all probability a β -glucoside, since it is the result of a type of synthesis which in all previous instances has led to β -glucosides, and since all the successive products are lævorotatory, whilst, in general, the α -glucosides are dextrorotatory.

Since amygdalin, the most important representative of the cyanogenetic glucosides, is a derivative of a disaccharide, the authors have extended the synthesis to similar sugars, and have prepared the compound of cellulose with glycollonitrile on lines similar to those used for linamarin.

Ethyl hepta-acetylcellosidoglycollate, needles, m. p. 161—163° (corr.), $[\alpha]_D^{17} - 30.9^\circ$ in acetone, is prepared from acetobromocellose, ethyl glycollate, and dry silver oxide, and is converted by methyl-alcoholic ammonia into *cellosidoglycollamide*, prisms, m. p. 150—152° (corr.), $[\alpha]_D^{17} - 27.9^\circ$ in water, which is hydrolysed by emulsin with the formation of dextrose. The amide is converted in the usual manner into *cellosidoglycollamide hepta-acetate*, slender needles, m. p. 205—206° (corr.), $[\alpha]_D^{18} - 20.6^\circ$ in acetone, which, when treated with phosphorus oxychloride, passes into *cellosidoglycollonitrile hepta-acetate*, small needles, m. p. 200—202° (corr.) after previous softening, $[\alpha]_D^{18} - 26.68^\circ$ in acetone. The latter, on deacetylation, gives *cellosidoglycollonitrile*, $\text{CN} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{C}_{12}\text{H}_{21}\text{O}_{10}$, which could only be obtained as an amorphous mass, frequently of a pale yellow colour; when heated, it softens at about 80°, and is slowly converted into a viscous mass, which evolves gas at about 108°. It has $[\alpha]_D^{18} - 28.74^\circ$ in water. When reacylated by acetic anhydride in pyridine solution, it gives the original hepta-acetate in good yield. It is hydrolysed by emulsin with comparative ease, giving hydrocyanic acid and dextrose. H. W.

Alkylaminochromi-compounds. III. H.J. MANDAL (*Ber.*, 1919, 52, [B], 330—341. Compare A., 1916, i, 202, 792).—The following *chloropentapropylaminochromic* salts are described: The *chloride*, $[\text{CrCl}(\text{NH}_2\text{Pr})_5]\text{Cl}_2$, is obtained by the action of propylamine on chromic chloride at as low a temperature as possible, a dichlorotetrapropylaminochromic chloride being formed if the reaction is not well controlled. It crystallises in red tablets from water, in which 1 part is soluble in 35 parts at the ordinary temperature, and it gives up propylamine at 60—70°. Other salts are prepared as precipitates from the red solution of the chloride by double decomposition or addition of a suitable chloride. The *bromide* requires nearly twice, and the *iodide* nearly three times, as much water for solution. The *mercurichloride*, $5\text{XCl}_2 \cdot 4\text{HgCl}_2$, is pale violet; the *mercuribromide*, XHgBr_4 , is very pale reddish-violet; the *mercuri-iodide*, XHgI_4 , is still paler; the *platinichloride*, $\text{XPtCl}_6 \cdot \text{H}_2\text{O}$, has the colour of chamois; the *bismuthichloride*, $\text{X}_3\text{Bi}_2\text{Cl}_{12}$, is a pale reddish-violet powder; and

the *stibichloride*, XSbCl_5 , forms very minute, indefinite crystals. The *hydrogen sulphate*, $\text{X}(\text{HSO}_4)_2$, crystallises in glistening, violet scales; the *dithionate*, XS_2O_6 , forms violet, hexagonal tablets; and the *sulphide*, XS_5 , is a yellowish-brown powder. The *nitrate*, $\text{X}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, forms long prisms. The *ferrocyanide*,



is pale red, but becomes yellowish-brown in the light, and is about the most insoluble salt of the series; the *ferricyanide*, $\text{X}_3(\text{FeC}_6\text{N}_6)_2$, is yellow with a tinge of red, and the *chromicyanide*, $\text{X}_3(\text{CrC}_6\text{N}_6)_2$, is a reddish-violet, microcrystalline powder. The *trioxalocobaltiate*, $\text{X}_3[\text{Co}(\text{C}_2\text{O}_4)_3]_2$, is a bluish-green, crystalline powder, and the *trioxalochromiate*, $\text{X}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]_2$, crystallises in brownish-violet, glistening bundles of minute needles. The dichromate is soluble, but the *chromate*, XCrO_4 , is a very sparingly soluble, yellow powder.

J. C. W.

Xanthates of Quaternary Ammonium, Sulphine, and Analogous Bases. JAIME FERRER (*Anal. Fis. Quim.*, 1918, **16**, 724—727).—Quaternary ammonium bases react with carbon disulphide in a manner similar to alkali hydroxides, giving xanthates. In a preliminary note, the author describes the preparation of the xanthates of quaternary ammonium, sulphine, and iodonium bases, giving some quantitative details of their properties. Tetramethylammonium hydroxide was dissolved in ethyl alcohol, and carbon disulphide added. On evaporation, the *xanthate* is obtained in yellow, hygroscopic needles, soluble in ether and acetone. With propyl alcohol, the corresponding xanthate is obtained in plates.

Phenyltrimethylammonium ethyl- and propyl-xanthates were prepared similarly, crystallising in needles. Solutions were obtained giving xanthate reactions by adding disulphide to alcoholic solutions of methylpyridinium hydroxide and methylveratrinium hydroxide.

Triethylsulphine hydroxide was dissolved in ethyl, propyl, and isobutyl alcohols. On treatment with carbon disulphide and evaporation, the corresponding *xanthates* were obtained in yellow needles soluble in water.

Diphenyliodonium hydroxide gives a *xanthate* crystallising in brilliant needles, only slightly soluble in water, alcohol, and ether.

By similar methods, *methylstibonium ethylxanthate* (colourless crystals) and *ethylmercury ethylxanthate* were prepared.

W. S. M.

Constitution of Methyloxaluric Acid. ROBERT BEHREND (*Ber.*, 1919, **52**, [B], 424—426).—Only one of the two possible methyloxaluric acids is known, but its constitution has not been determined hitherto (compare Henkel, A., 1911, i, 159). Its ethyl ester, flat prisms, m. p. 144—146°, has now been heated with acetyl chloride in a sealed tube at 120—130°, and the following products have been isolated and fully identified: (a) much methylparabanic acid, (b) a small quantity of the acetyl derivative of this, and

(c) a little acetoxamethane. The last substance gives the clue to the constitution of the methyloxaluric acid, for it may be supposed to be formed according to the equation $\text{NHMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{CO}_2\text{Et} + \text{AcCl} = \text{NHAc}\cdot\text{CO}\cdot\text{CO}_2\text{Et} + \text{CH}_3\cdot\text{N}\cdot\text{CO} + \text{HCl}$.
J. C. W.

Action of Halogenates and Hypohalogenites on Mercury Fulminate. A. LANGHANS (*J. pr. Chem.*, 1918, [ii], **98**, 255—314). —The action of halogenates and hypohalogenites on mercury fulminate has been studied under various conditions; more definite quantitative data are promised in a subsequent paper, but the results already obtained are considered to furnish further evidence for the oxime structure for fulminic acid.

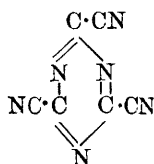
The action of potassium chlorate and potassium bromate solutions on mercury fulminate in the presence of hydrochloric acid depends greatly on the conditions of the experiment, and the original memoir must be consulted for details. Generally, it may be said that bromate acts more energetically than chlorate, and that for the production of the maximum amount of blue, oily product a definite relationship between the concentrations of hydrochloric acid and bromate must be maintained, and that the quantity of mercury fulminate is definitely related to that of the other reagents.

Mercury fulminate is decomposed by potassium hypochlorite solution, yielding chiefly mercuric oxide, which is only produced in small amount by hypobromite or hypoiodite. The action of potassium hypobromite yields varying products, according to experimental conditions, a summary of which is impossible until more exact data have been obtained; the most remarkable product is a deep blue oil, which is best obtained by the gradual addition of moist mercury fulminate to a solution of bromine in 10% potassium hydroxide, 7—8 c.c. of bromine being used for each 10 grams of potassium hydroxide; it has D 2.6844 or 2.6852, and is unstable towards light, but more stable in the dark. It consists in all probability of *bromonitrosomethane*. It decomposes when distilled under ordinary pressure, evolving brown vapours and yielding distillates, which generally crystallise after a time. It yields crystalline *products* when treated with the following reagents: sodium sulphite or sodium hydrogen sulphite (colourless leaflets, m. p. 91—92° [uncorr.] after softening at 89°); sodium thio-sulphate; potassium cyanide (m. p. 55°); ammonium persulphate (m. p. 68°); silver nitrate (colourless leaflets, m. p. 67°); phenylhydrazine; furfuraldehyde (m. p. above 200°); benzoyl peroxide (colourless needles); hexamethylenetetramine (yellow or white solid, m. p.'s 95° and 187° respectively, according to conditions of experiment); benzenesulphonic acid; picric acid; sodium xanthogenate; glycine (m. p. 65°). The blue compound is not formed when bromine acts on mercury fulminate in the presence of acetic anhydride, glacial acetic acid, or pyridine.

A sensitive method for the detection of mercury fulminate in fuse compositions is founded on the production of the blue oil.

H. W.

Simple Cyanic and Cyanuric Compounds. I. Hexacyanogen [Cyanuric Cyanide]. ERWIN OTT (*Ber.*, 1919, **52**, [B], 656—665).—*Hexacyanogen* (annexed formula) is obtained by heating a mixture of cyanuric tricarboxylamide and phosphoric oxide in a vacuum rapidly to 210—220°, and finally to about 250°. The yield is about 17%.



The substance forms monoclinic crystals ($a:b:c = 0.9233:1:1.0688$, $\beta = 90^\circ 26'$), has m. p. 119° , b. p. 262° (corr.)/771 mm., $119^\circ/0.5\text{—}1$ mm. It separates from benzene + $1\text{C}_6\text{H}_6$. When the vapour is led over a strongly heated platinum wire, it is quantitatively depolymerised to dicyanogen. It is very sensitive to moisture. It slowly dissolves in water at 0° , and two cyanogen groups are rapidly eliminated in the form of hydrogen cyanide, whilst the third cyanogen group is removed at a slightly higher temperature, cyanuric acid being formed. In virtue of the three conjugated double linkings, it seems probable that water is first added and hydrogen cyanide subsequently eliminated from the hydroxynitrile thus formed. With methyl alcohol, reaction proceeds more slowly, and can be arrested by suitable adjustment of experimental conditions at any of the three stages theoretically possible. There are thus obtained: (1) the *monomethoxydinitrile*, $\text{OMe} \cdot \text{C}_3\text{N}_3(\text{CN})_2$, colourless leaflets, m. p. 86.5° , (2) the *dimethoxymononitrile*, prisms, m. p. 21° , and (3) trimethyl cyanurate, m. p. 135° . A solution of hexacyanogen in carbon tetrachloride does not visibly react with chlorine even in the presence of iodine, but the odour of cyanuric chloride shows some action to occur; it also appears to be indifferent to hydrogen chloride.

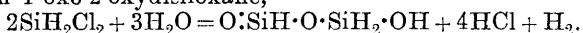
H. W.

Silicon Hydrides. VI. Chlorination and Methylation of Monosilane. ALFRED STOCK and CARL SOMIESKI (*Ber.*, 1919, **52**, [B], 695—724. Compare *A.*, 1916, ii, 319; 1917, ii, 110, 111, 353, 361).—Whilst monosilane does not react with hydrogen chloride in the absence of a catalyst at 200° , reaction occurs slowly in the presence of aluminium chloride at the ordinary temperature, and with reasonable rapidity at 100° ; when the gases are used in molar proportions, the chief product is monochlorosilane, whilst with the double proportion of hydrogen chloride, *dichlorosilane* is chiefly formed, the action in this respect differing somewhat considerably from that with hydrogen bromide.

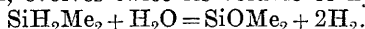
Chloromonosilane is a non-spontaneously inflammable gas, m. p. -118° , b. p. -30.5° , $D_{-113^\circ} 1.145$ (as liquid). It is immediately decomposed by water, yielding disiloxane; protracted action of water causes hydrolysis with evolution of hydrogen. It reacts with gaseous zinc methyl, yielding exclusively *methylmonosilane*, SiH_3Me , b. p. -57° , m. p. -156.5° , which is scarcely attacked by water in the absence of alkali, but is slowly decomposed by alkali in accordance with the equation $\text{SiH}_3\text{Me} + 2\text{H}_2\text{O} = [\text{SiO}(\text{OH})\text{Me}]_x +$

3H_2 . Further chlorination of methylsilane by means of hydrogen chloride and aluminium chloride leads to the production of *methylchloromonosilane* and *methyldichloromonosilane*, which can be separated by protracted fractional distillation. The former is a colourless gas, m. p. 134° , b. p. $\text{ca} + 7^\circ$, $D_{-8^\circ} 0.935$ (as liquid), which is very sensitive to moisture; evidence that the chlorine atom is attached to silicon is afforded by converting it into dimethylsilane by the action of zinc methyl, the product being identical with that prepared from dichlorosilane. Dichloromethylmonosilane was isolated in approximately pure condition.

Dichloromonosilane is obtained as a by-product in the preparation of the monohalogen derivative by further chlorination of chloromonosilane by aluminium chloride and hydrogen chloride, and by the action of hydrogen chloride (2 mols.) on monosilane (1 mol.); in the latter case, the main product is the dichloro-derivative mixed with a little monochloro-product and unchanged hydrogen chloride and very little trichloromonosilane. It has m. p. -122° , b. p. 8.5° , and is particularly sensitive to moisture and fat. With water, it immediately yields prosiloxane, $\text{SiH}_2(\text{O})$, and then 1-oxo-2-oxydisiloxane,



It is converted by thorough treatment with gaseous zinc methyl into dimethylmonosilane, SiH_2Me_2 , m. p. -150° , b. p. -20° , which, with alkali, evolves twice its volume of hydrogen,



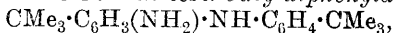
The dimethylprosilo-xane is soluble in an excess of alkali, probably yielding $\text{SiMe}_2(\text{ONa})_2$; acids precipitate an oil from this solution which slowly becomes partly solid, and consists of a mixture of SiMe_2O , $\text{SiMe}_2(\text{OH})_2$, and their condensation and polymerisation products.

It is noticeable that the displacement of hydrogen by chlorine in silicon derivatives has much less influence in raising the boiling and melting points than with derivatives of carbon. H. W.

Nitration of *tert*-Butylbenzene. D. F. DU TOIT MALHERBE (*Ber.*, 1919, **52**, [B], 319—324).—When *tert*-butylbenzene is left with nitric acid ($D_{15} 1.5$), it is almost entirely converted into *p*-nitro-*tert*-butylbenzene, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CMe}_3$, an oil which does not crystallise in a freezing mixture, having b. p. $142\text{--}143^\circ/17\text{ mm.}$, whilst a dinitro-derivative, pale yellow prisms, m. p. $61\text{--}62^\circ$, b. p. $185^\circ/15\text{ mm.}$, is formed at 60° (Baur, A., 1894, i, 445).

The constitution of the mono-nitro-compound does not agree with Senkowski's statements (A., 1890, 1296). It has been proved as follows: (a) oxidation with dilute nitric acid at 130° to *p*-nitrobenzoic acid; (b) reduction to *p*-*tert*-butylaniline, and conversion into its acetyl, benzoyl, and dimethyl derivatives, and into *p*-*tert*-butylphenol; (c) reduction by sodium methoxide solution to *p*-azoxy-*tert*-butylbenzene, pale yellow leaflets, m. p. 138° ; (d) reduction to *p*-azo-*tert*-butylbenzene, orange-red needles, m. p. 183° , and the hydrazo-compound by means of aqueous-alcoholic

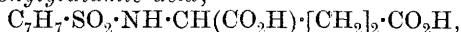
potassium hydroxide and zinc dust; (e) the semidine transformation of the hydrazo-derivative, by means of alcoholic stannous chloride, into 6-amino-3:4'-di-tert.-butyldiphenylamine,



white leaflets, m. p. 100—101°. As an *o*-aminodiphenylamine, the latter base reacts with benzil to form a stilbazonium compound, $\text{C}_{34}\text{H}_{36}\text{ON}_2$, greenish-yellow needles, m. p. 165—167° (Taüber, A., 1892, 853), and with benzaldehyde to give a *benzenyl* compound, $\text{C}_{27}\text{H}_{32}\text{N}_2$, slender, yellow needles, m. p. 126—127° (*ibid.*).

J. C. W.

New Compounds of Glutamic Acid. PETER BERGELL (*Zeitsch. physiol. Chem.*, 1919, **104**, 182—188).— β -Naphthalenesulphonylglutamic acid, $\text{C}_{10}\text{H}_7\text{SO}_2\text{NH}\cdot\text{CH}(\text{CO}_2\text{H})\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{H}$, crystallises in microscopic needles from water, m. p. 165° (uncorr.).
Toluenesulphonylglutamic acid,



forms woolly masses of soft, short needles, m. p. 115—117° (uncorr.). The presence of 1% of glutamic acid or glycine in urine may be detected by the isolation of their β -naphthalenesulphonyl derivatives.

J. C. D.

Formation of Diphenyl by the Action of Cupric Salts on Organometallic Compounds of Magnesium. JACOB KRIZEWSKY and EUSTACE EBENEZER TURNER (*T.*, 1919, **114**, 559—561).

Transformation of Quaternary Ammonium Salts into Tertiary Amines with Sodium Ethoxide. D. VORLÄNDER and ELISABETH SPRECKELS (*Ber.*, 1919, **52**, [B], 309—311).—Aromatic primary amines can be readily converted into a mixture of the dimethyl derivatives and the corresponding quaternary salts by treatment with an excess of methyl sulphate and alkali. A convenient process for transforming the quaternary salts into the tertiary bases has now been found. The crude product is saturated with hydrochloric acid, evaporated to dryness, and the mixed salts are boiled under reflux with a solution of sodium (two or three equivalents) in alcohol (50—100 parts) for three to five hours. From 85 to 95% of the quaternary salt is converted into the tertiary amine.

The process has not been fully tested in the case of aliphatic bases, but more concentrated solutions of sodium ethoxide, or perhaps amyloxide, appear to be necessary.

J. C. W.

Oxidation of *o*-Tolyltrimethylammonium Salts to *o*-Benzobetaine. D. VORLÄNDER and FRANZ JANECKE (*Ber.*, 1919, **52**, [B], 311—314).—The oxidation of *o*-tolyltrimethylammonium methyl sulphate (Ullmann, A., 1903, i, 395) to *o*-benzobetaine (Willstätter, A., 1904, i, 235) by means of permanganate is described. In addition to the hydriodide, aurichloride, and free base already obtained by Willstätter, the authors have prepared the *hydro*-

chloride, $C_{10}H_{14}O_2NCl \cdot H_2O$, jagged leaflets, m. p. 170—176°. When boiled with a solution of sodium ethoxide, the base deposits the sodium salt of *N*-dimethylantranilic acid in felted needles. The free acid corresponds with Willstätter's description (*ibid.*), and forms a *hydriodide*, m. p. 180° (decomp.), a *periodide*, m. p. 163° (decomp.), and a *platinichloride*, m. p. 198° (decomp.).

J. C. W.

Nitration of Benzotrichloride. ELISABETH SPRECKELS (*Ber.*, 1919, **52**, [B], 315—319).—Under the usual conditions of nitration, benzotrichloride yields nitrobenzoic acids, but if treated with a solution of nitrogen pentoxide in carbon tetrachloride at -10° , a mixture of nitrobenzotrichlorides is formed almost free from nitrobenzoic acids and unchanged material. About 80% of the mixture has b. p. 150—153°/18 mm. It is fairly stable towards water and cold dilute alkalis, much more so, in fact, than benzotrichloride itself, neither does it readily change into the nitrobenzoic acids in contact with cold, concentrated nitric acid. It is not, therefore, the precursor of the nitrobenzoic acids formed under the usual conditions.

The proportions of the isomerides in the mixture have been determined approximately by boiling with barium hydroxide and separating the barium salts of the nitrobenzoic acids. The main product is *m*-nitrobenzotrichloride, with about one-fifth of its weight of the *para*-compound, which is much more than benzoic acid yields. There is also a small quantity of the *ortho*-compound in the mixture.

J. C. W.

Phenylcarbamic Acid and its Homologues. F. E. C. SCHEFFER (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 664—677).—The compound formed between aniline and carbon dioxide under pressure at low temperatures was examined by Ditte many years ago (*A.*, 1888, 49), and was found to contain the constituents in equimolecular proportions. This composition has now been confirmed and the conditions of its existence established. Within the limits of temperature and pressure of the experiments, four phases are possible—the solid compound, two liquids, and vapour. The four three-phase *P.-T.* curves have been determined and the point of intersection, the quadruple point, found at 18° with a pressure of 52.0 atm. The critical end-point lies at 37°, that is, 6° and about 7 atm. higher than the critical point of carbon dioxide.

Similar compounds are formed between carbon dioxide and the three toluidines. The quadruple points of the three compounds are as follows: *o*-toluidine, -7.5° , 27.5 atm.; *m*-toluidine, 6.3° , 39.2 atm.; *p*-toluidine, (1) 31.5° , 70 atm., (2) 29.7° , 44 atm. In the last case, there are two quadruple points; the first has the compound as the solid phase, whilst the second has *p*-toluidine and the compound both present as solid phases in equilibrium with one liquid and vapour. Whilst *o*-toluidine has the lowest quadruple

point, *m*-toluidine has the lowest melting point, but otherwise the quadruple and melting points follow the same order. The critical end-points lie close together, and the three-phase curves L_1L_2G (two liquids and vapour) are nearly coincident.

All the compounds contain base and carbon dioxide in molecular proportions, and are to be regarded as carbamic acids.

E. H. R.

Preparation of Phenol. H. H. Dow (U.S. Pat. 1274394).—Bromobenzene is converted into phenol by heating with a dilute alkali hydroxide solution in closed vessels under a pressure of 20 atmospheres. [See *J. Soc. Chem. Ind.*, June.] G. F. M.

Some Aromatic Amines and Chloroacetyl Derivatives. WALTER A. JACOBS, MICHAEL HEIDELBERGER, and IDA P. ROLF (*J. Amer. Chem. Soc.*, 1919, **41**, 458—474).—The compounds described in this communication are intermediate products in the preparation of several aromatic arsenic derivatives, which will be dealt with in a future series of papers.

An improved method for preparing *o*-chloroacetylaminophenol is described (compare A., 1915, i, 668). Its *acetate*,



obtained by the action of acetic anhydride and a drop of sulphuric acid, has m. p. 113·5—114·5°.

4-Chloroacetyl-amino-*o*-cresol, rhombic plates, m. p. 154—155°, and the more soluble 6-chloroacetyl-amino-*p*-cresol, silky needles, m. p. 151—152·5°, are prepared from the aminocresols by the new way (A., 1917, i, 552).

1-Chloroacetyl-amino- β -naphthol forms very pale yellow, nacreous plates, m. p. 192—193° (decomp.), and 4-chloroacetyl-amino- α -naphthol crystallises in long, faintly purple, silky needles, m. p. 199·5—201·5°.

4:6-Dichloro-3-acetylaminophenol is obtained in silky needles, m. p. 233—236°, by chlorinating *m*-acetylaminophenol in acetic acid solution, and is hydrolysed by boiling with hydrochloric acid to 4:6-dichloro-3-aminophenol, large, striated prisms, m. p. 135—136°, which is converted into 4:6-dichloro-3-chloroacetylaminophenol, slender, interlaced needles, m. p. 185·5—186·5°. The 4:6-dichloro-3-acetylaminophenol is also methylated by means of methyl sulphate, and the 4:6-dichloro-3-acetanisidide, tufts of delicate needles, m. p. 157·5—159°, is hydrolysed to 4:6-dichloro-3-anisidine, which crystallises in creamy, rhombic prisms, m. p. 50·5—51·5° (corr.). The constitution of the compounds of this series is revealed by converting the latter base, by the diazo-reaction and application of methyl sulphate, into 4:6-dichloro-1:3-dimethoxybenzene (Auwers and Pohl, A., 1914, i, 981).

If the chlorination of *m*-acetylaminophenol is carried out without the precaution of shaking the acetic acid mixture, a good deal of 2:4:6-trichloro-3-acetylaminophenol is formed. This separates when the dilute acetic acid mother liquors from the dichloro-com-

pound are further diluted, and it crystallises in rhombic plates with $0.5\text{H}_2\text{O}$, or anhydrous needles, m. p. $185\text{--}186.5^\circ$.

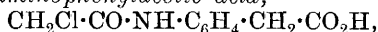
6-Bromo-3-acetylaminophenol is prepared by direct bromination and hydrolysed to 6-bromo-3-aminophenol (compare Heller, A., 1909, i, 568). 6-Bromo-3-chloroacetylaminophenol crystallises in rhombs, m. p. $191\text{--}193^\circ$.

m-Acetylaminophenol is also boiled with chloroacetic acid and concentrated sodium hydroxide, and thus converted into *m*-acetylaminophenoxyacetic acid, $\text{NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, which crystallises from water in slender needles with $1\text{H}_2\text{O}$, or from acetic acid in spherules, m. p. $170.5\text{--}172.5^\circ$. This is hydrolysed to *m*-aminophenoxyacetic acid (A., 1917, i, 695), and then converted into *m*-chloroacetylaminophenoxyacetic acid, spherules, m. p. $159\text{--}160^\circ$ (clear at 162°).

Considerable quantities of 4-aminoguaiacol were required for the preparation of catechol derivatives. This is obtained by coupling diazotised sulphanilic acid with guaiacol and reducing the crude dye with hydrogen sulphide in ammoniacal solution. *p*-Sulphobenzeneazoguaiacol crystallises from water in glistening, green needles and long, thin plates with $1\text{H}_2\text{O}$, decomp. above 220° . 4-Aminoguaiacol is hydrolysed by means of hydrobromic acid to the *hydrobromide* (flat needles or plates, decomp. $255\text{--}260^\circ$) of 4-aminocatechol, which crystallises from a mixture of alcohol and benzene in grey plates and clusters of short prisms, m. p. $124\text{--}125^\circ$ (decomp., purple residue). In the isolation and filtration of the base, air must be excluded as far as possible by a current of carbon dioxide. 4-Chloroacetylaminocatechol, $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_3(\text{OH})_2$, forms slender needles, m. p. $156\text{--}157.5^\circ$.

p-Chloroacetylaminooacetophenone crystallises as a woolly mass of needles from alcohol or leafy aggregates of plates from toluene, m. p. $152\text{--}153^\circ$ (corr.).

p-Chloroacetylaminophenylacetic acid,



forms a snowy mass of needles, m. p. $158\text{--}160^\circ$.

Ethyl chloroacetylthranilate, $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Et}$, crystallises in glistening needles, m. p. $79.5\text{--}80^\circ$ (corr.), and changes into *ethyl iodoacetylthranilate*, transparent prisms, m. p. $78.5\text{--}79^\circ$ (corr.), when warmed with a solution of sodium iodide in acetone. *o*-Methylaminobenzoic acid yields *chloroacetyl-N-methylthranilic acid*, $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, colourless spears, m. p. $167\text{--}168^\circ$ (corr.), the *ethyl* ester of which forms stout prisms, m. p. $50\text{--}51^\circ$ (corr.).

Sodium sulphanilate gives rise to *sodium chloroacetylsulphanilate*, $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{Na}$, which crystallises in hair-like masses of needles, decomposing somewhat when dried at 100° .

3-Amino-*o*-phenolsulphonic acid, prepared by heating *m*-aminophenol with concentrated sulphuric acid at 100° , yields 3-chloroacetyl-amino-*o*-phenolsulphonic acid, minute plates and flat needles, not molten at 275° , the *sodium* salt of which crystallises as a voluminous mass of small needles with $0.5\text{H}_2\text{O}$.

Improvements in the preparation of chloroacetomethylamide and chloroacetopiperidide are described (compare A., 1915, i, 668). *Chloroaceto-n-propylamide*, $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NHPr}^a$, has b. p. $105\text{--}106^\circ/10\cdot5$ mm. (corr.), and forms a *hexamethylenetetraminium* salt, in stout, hexagonal plates, m. p. $147\text{--}149^\circ$.

Ethylcarbamide yields *chloroacetyl ethylcarbamide*,
 $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NHEt}$,
 in long needles, m. p. $141\cdot5\text{--}142\cdot5^\circ$ (corr.). J. C. W.

Catalytic Preparation of the Aminophenols and the Phenylenediamines. O. W. BROWN and L. L. CARRICK (*J. Amer. Chem. Soc.*, 1919, **41**, 436—440).—Mignonac (*Bull. Soc. chim.*, 1910, [iv], **7**, 270) described the reduction of the nitrophenols by passing a mixture of their vapours and hydrogen over nickel at $160\text{--}190^\circ$, but found that the production of the aminophenols was accompanied by the formation of ammonia, phenol, and aniline. This work is confirmed, and it is also reported that nickel is not so active when deposited on pumice as otherwise.

With finely divided copper, deposited on small pieces of pumice, the reduction is more efficient than with nickel, there being no by-products. Thus *o*- or *p*-nitrophenol and hydrogen passed over copper at $210\text{--}315^\circ$ (best, 265°) give practically quantitative yields of the pure white aminophenols, the more volatile product, of course, reacting more quickly. The *o*-aminophenol is obtained in plates when copper is used, but when reduced nickel is employed, it is formed in long needles with the same m. p. (170°), especially at the higher ranges of temperature.

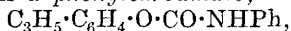
The nitroanilines, and especially *m*-dinitrobenzene, may be reduced in the same way to the phenylenediamines, but the process is too slow (owing to the slight volatility of the compounds) to be of much practical value, the only advantage being the high degree of purity of the products. J. C. W.

Transformation of Phenyl Allyl Ethers into the Isomeric Allylphenols. II. L. CLAISEN (*Annalen*, 1919, **418**, 69—120. Compare A., 1912, i, 965; 1913, i, 1175).—I. *Mono-, Di-, and Tri-allylation of Phenol* [with O. EISLEB and F. KREMERs].—*o*-Allylphenol, b. p. $220^\circ/760$ mm. or $99^\circ/12$ mm., D_{15}^{25} $1\cdot0255$, is obtained (1) by heating phenyl allyl ether in an atmosphere of carbon dioxide until the temperature is about 220° , heating for about six hours being necessary. (2) by heating 4-allyloxybenzoic acid with quinoline at 170° , and finally at the b. p. of the solution, (3) by heating 3-allylsalicylic acid with dimethylaniline slowly to the b. p. of the solution, (4) by boiling a mixture of methyl 3-allylsalicylate and aniline for four hours, and (5) least satisfactorily from 2-allyloxybenzoic acid. In the first method, a small quantity of 1-methylcoumaran is formed, which is removed by extraction with light petroleum after basifying the reaction product with 20% sodium hydroxide. Attempts to accelerate the transformation of phenyl allyl ether into *o*-allylphenol by catalysts were unsuccessful; alkalis had no effect, and acids only increased the amount of methyl-

coumaran, the addition of pyridine hydrochloride, for example, resulting in the production of this compound in 60% yield.

The position of the allyl group in *o*-allylphenol is proved (1) by heating with methyl-alcoholic potassium hydroxide, whereby Pauly and Buttler's *o*-propenylphenol is obtained, (2) by heating the methyl ether of the allylphenol with potassium hydroxide and oxidising the resulting *o*-propenylphenyl methyl ether, whereby *o*-methoxybenzoic acid is obtained, and (3) by coupling allylphenol with benzenediazonium chloride, the product being identical with the 4-benzeneazo-2-allylphenol obtained by the transformation of 4-benzeneazophenyl allyl ether (*loc. cit.*).

o-Allylphenol forms a *phenylcarbamate*,



colourless needles, m. p. 106—106·5°, *methyl ether* (*o*-esdragole), b. p. 207°/761 mm. or 86—87°/12 mm., D_{15}^{25} 0·9770 (the *ozonide* of which is very explosive and yields *o*-methoxyphenylacetaldehyde by treatment with glacial acetic acid and zinc dust), and *acetate*, b. p. 238·5—239°/757 mm. or 117—118°/15 mm.; the last derivative forms an oily *dibromide*, which is converted into 1-methylcoumarone by boiling with methyl-alcoholic potassium hydroxide.

To the list of substitution products of *o*-allylphenol already described (*loc. cit.*) is to be added 4:6-dichloro-*o*-allylphenol, b. p. 264°, D_{15}^{25} 1·288, which is very easily obtained by heating 3:5-dichloro-2-allyloxybenzoic acid, needles, m. p. 118° (decomp.); the *methyl ester* of this acid, $\text{C}_3\text{H}_5\cdot\text{O}\cdot\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{CO}_2\text{Me}$, b. p. 160°/10 mm., is prepared by boiling methyl 3:5-dichlorosalicylate in methyl ethyl ketone solution with allyl bromide and potassium carbonate.

o-Propylphenol is obtained by reducing *o*-allylphenol by the Paal-Skita method, and also by reducing 3-allylsalicylic acid in a similar manner and heating the resulting 3-propylsalicylic acid, m. p. 91·5° (Spica gives 93—94°), with dimethylaniline at the b. p. of the solution until the evolution of carbon dioxide ceases. 2-Acetoxy-3-propylbenzoic acid (3-propylaspirin) crystallises in needles, m. p. 97—97·5°.

2:6-Diallylphenol, b. p. 256—257°/770 mm. (slight decomp.; in carbon dioxide) or 130°/15 mm., has D_{15}^{25} 0·9920, not 0·9905, as stated previously (*loc. cit.*). It is readily obtained by heating *o*-allylphenyl allyl ether, b. p. 104—105°/10 mm., D_{15}^{25} 0·9675 (prepared from *o*-allylphenol in acetone solution, allyl bromide, and potassium carbonate), for ten minutes in an atmosphere of carbon dioxide while the temperature rises from 235° to 256°, or, better, with half its weight of diethylaniline for thirty minutes while the temperature increases from 225° to 237°. It forms a *phenylcarbamate*, needles, m. p. 141—142°. Its constitution is definitely proved by the production of the compound by heating 4-hydroxy-3:5-diallylbenzoic acid (*loc. cit.*) with dimethylaniline at the b. p. for one to one and a-half hours. By hydrogenation in alcoholic solution, 2:6-diallylphenol yields 2:6-dipropylphenol, b. p. 256°/764 mm., m. p. 28° (*phenylcarbamate*, needles, m. p. 125°).

4-Allylphenol and 2:4-diallylphenol are not produced by the transformation of phenyl allyl ether and *o*-allylphenyl allyl ether respectively. The latter, b. p. 266—268°/750 mm. (*phenylcarbamate*, prisms, m. p. 88—88·5°), is obtained indirectly by heating 3:5-diallylsalicylic acid (*loc. cit.*) with dimethylaniline at the b. p. for thirty to forty-five minutes. 3:5-Dipropylsalicylic acid, needles, m. p. 100—100·5°, obtained by reducing 3:5-diallylsalicylic acid in alcoholic solution by the Paal-Skita method, is converted by boiling with dimethylaniline into 2:4-dipropylphenol, b. p. 263°/747 mm. or 130°/11 mm., D_{25}^{15} 0·9350 (*phenylcarbamate*, needles, m. p. 131°).

2:6-Diallylphenyl allyl ether, b. p. 132·5—134°/11 mm., D_{15}^{15} 0·9548, is prepared by heating an alcoholic solution of 2:6-diallylphenol with allyl bromide and potassium carbonate on the water-bath for ten hours. When it is heated in a current of carbon dioxide until the temperature rises from about 250° to about 290°, or, better, when it is boiled with half its weight of diethylaniline for fifteen minutes until the temperature rises from 225° to 248°, it is transformed into 2:4:6-triallylphenol (*loc. cit.*), b. p. 293—295°/760 mm. or 158—159°/14 mm., D_{15}^{15} 0·9785.

The influence of the b. p. of an allyl ether on the rapidity of its transformation into the allylphenol (*loc. cit.*) is well illustrated by the production of *o*-allylphenol, 2:6-diallylphenol, and 2:4:6-triallylphenol from the respective allyl ethers. The first reaction requires about six hours, the second proceeds much more rapidly, and the third almost instantly. It is to be noted, however, that the quantity of resinous matter produced is greater the higher is the temperature of transformation. The formation of this by-product is greatly diminished by heating in an atmosphere of hydrogen or carbon dioxide, or, best of all, by boiling the ether with dimethyl- or diethyl-aniline. The basic nature of this solvent appears to be of influence, since an indifferent, non-basic solvent of similar b. p. effects a much less satisfactory transformation.

cycloHexanol allyl ether, b. p. 169—172°/740 mm., D_{15}^{15} 0·8960, obtained by warming a benzene solution of cyclohexanol with sodium for one day and then boiling with allyl bromide, cannot be transformed into allylcyclohexanol.

II. Nitroso- and Amino-derivatives of Monoallylphenol and Diallylphenol [with F. KREMERS].—These two phenols yield nitroso-derivatives very smoothly. 4-Nitroso-2-allylphenol (2-allyl-p-benzoquinone-4-oxime), $\text{OH}\cdot\text{N}:\text{C}_6\text{H}_3(\text{C}_3\text{H}_5):\text{O}$, leaflets, m. p. 100—101° (decomp.), is obtained in the form of its sodium salt, garnet needles, by keeping a mixture of *o*-allylphenol, amyl nitrite, and concentrated methyl-alcoholic sodium methoxide solution for one day at the ordinary temperature and one day at 0°. The sodium salt, by warming on the water-bath for ten minutes with zinc dust and a cold, saturated solution of ammonium carbonate, or by treatment below 30° with hydrogen sulphide, a solution of ammonium chloride containing 25% aqueous ammonia being used as solvent,

is reduced to 4-amino-2-allylphenol, leaflets, m. p. 113·5—114°, the N-acetyl derivative of which forms leaflets, m. p. 93°.

4-Nitroso-2:6-diallylphenol (2:6-diallyl-p-benzoquinone-4-oxime), leaflets, m. p. 142—143°, obtained in a similar manner from 2:6-diallylphenol (a sodium salt is not precipitated in this case), yields 4-amino-2:6-diallylphenol, flattened prisms, m. p. 78·5°, by reduction with ammonium sulphide and concentrated aqueous ammonia.

III. *The Allyl Ether Transformation of Aminophenols* [with F. KREMERS].—*p*-Acetylaminophenol (used in preference to *p*-aminophenol to avoid allylation at the nitrogen atom) is boiled with acetone, allyl bromide, and potassium carbonate, and the resulting *p*-acetylaminophenyl allyl ether, leaflets, m. p. 93°, is boiled with dimethylaniline for six hours in a slow current of hydrogen, whereby the 4-acetyl-amino-*o*-allylphenol, m. p. 93°, described above is obtained; its *ethyl ether*, $\text{NHAc} \cdot \text{C}_6\text{H}_3(\text{C}_3\text{H}_5) \cdot \text{OEt}$, colourless leaflets, m. p. 121·5°, shows a very slight antipyretic action in comparison with phenacetin. By treatment with fuming hydrobromic acid, 4-acetyl-amino-*o*-allylphenol is converted into 4-acetyl-amino-1-methylcoumaran, $\text{NHAc} \cdot \text{C}_6\text{H}_3 \left\langle \begin{smallmatrix} \text{O} \\ \text{CH}_2 \end{smallmatrix} \right\rangle \text{CHMe}$, colourless needles, m. p. 127—127·5°. By boiling for one hour with 10% hydrochloric acid or 25% sulphuric acid, *p*-acetylaminophenyl allyl ether is converted into the *hydrochloride*, leaflets, m. p. 212°, or the *sulphate* of *p*-aminophenyl allyl ether, both of which are very sparingly soluble in water. *p*-Aminophenyl allyl ether is converted into 4-amino-*o*-allylphenol (above) by heating with petroleum (b. p. 185°) for six hours in a current of hydrogen, and the latter into 4-amino-*o*-propenylphenol, $\text{NH}_2 \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{CH} : \text{CHMe}$, silvery leaflets, m. p. about 172° (rapidly heated) or 168° (slowly heated), by boiling with very concentrated methyl-alcoholic potassium hydroxide in a slow current of hydrogen. The propenyl compound is more conveniently obtained by submitting 4-acetyl-amino-*o*-allylphenol to the same treatment.

4-Acetyl-amino-*o*-allylphenol is converted by boiling acetone, allyl bromide, and potassium carbonate into 4-acetyl-amino-*o*-allylphenyl allyl ether, colourless leaflets, m. p. 111·5—112°, which yields 4-acetyl-amino-2:6-diallylphenol, leaflets and needles, m. p. 85—86°, by treatment by the dimethylaniline method; from the latter, 4-amino-2:6-diallylphenol (above) is obtained, but not satisfactorily, by boiling with dilute sulphuric acid in an atmosphere of hydrogen.

IV. *Synthesis of Eugenol* [with F. KREMERS].—Methyl guaiacol-carboxylate (3-methoxysalicylate), m. p. 66—66·5° (Fritsch gives 63°; Einhorn, 73°), is converted by boiling with methyl ethyl ketone, allyl bromide, potassium carbonate, and a little potassium iodide for seven hours into methyl 3-methoxy-2-allyloxybenzoate, b. p. 165—167°/8 mm., which yields the corresponding acid, $\text{C}_{11}\text{H}_{12}\text{O}_4$, needles, m. p. 65°, by hydrolysis with boiling 30% methyl-

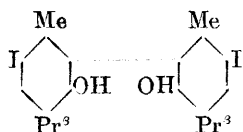
alcoholic potassium hydroxide. When heated, the acid loses carbon dioxide and suffers transformation, yielding *o*-eugenol almost exclusively, but its methyl ester is converted almost explosively at 230—240° into *methyl 6-hydroxy-5-methoxy-3-allylbenzoate*, needles, m. p. 55—55·5°, b. p. 173—174°/12 mm. On account of the violence of the transformation, a method of heating under diminished pressure (in this case 200°/60 mm.) was tried, and gave such satisfactory results that it is recommended for the transformation of other allyl ethers into allylphenols. On hydrolysis, the preceding ester yields *6-hydroxy-5-methoxy-3-allylbenzoic acid*, prisms, m. p. 127° (hydrated, m. p. 85—88°), which is converted into eugenol by heating with dimethylaniline at 160°; the methyl ester also yields eugenol (and methylaniline) by boiling with aniline for four hours.

C. S.

The Aristols and the Quantitative Estimation of Thymol.

E. MOLES and M. MARQUINA (*Anal. Fis. Quim.*, 1919, **17**, 59—83).

—Aristol is obtained as a red precipitate on adding a solution of iodine in potassium iodide to an alkaline solution of thymol (Messinger and Vortmann, A., 1889, 1150). On drying, the red substance loses water and iodine and passes into a yellow powder, one molecule of aristol giving 75 molecules of water and 0·15 atom of iodine. The freshly precipitated substance appears to behave as a gel in which iodine is adsorbed. The m. p. of both forms varies between 105° and 115°. A possible quinonoid or ketone structure was tested by means of hydriodic acid and by phenylhydrazine with negative results. Determinations of the molecular weight by cryoscopic measurements in benzene and thymol show that double molecules are present in the former solvent and single in the latter, the polymerisation indicating a phenolic structure. The constitution assigned to the yellow aristol is di-iododithymol (annexed formula). The following method



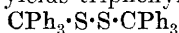
for the estimation of thymol is given: The thymol, dissolved in water, is added to sodium hydrogen carbonate solution. A measured quantity of standard iodine solution in excess is added, and the mixture is acidified with sulphuric or hydrochloric acid. The excess of iodine is titrated with thiosulphate solution. Over wide ranges of variation in the value of the ratios thymol:sodium hydrogen carbonate and thymol:iodine added, the mean value of the quantity of iodine consumed was 3·60 atoms per molecule of thymol.

W. S. M.

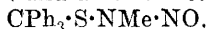
Triphenylmethyl Sulphur Compounds. D. VORLÄNDER and ERNST MITTAG (*Ber.*, 1919, **52**, [B], 413—423. Compare A., 1913, i, 1335).—A poor yield of *triphenylmethyl sulphide*, $S(CPh_3)_2$, may be obtained by the interaction of triphenylchloromethane and alcoholic sodium sulphide or sodium triphenylmethyl sulphide, $CPh_3\cdot SNa$. It is a white powder, m. p. 182° (decomp.), which only

reacts with alcoholic mercuric cyanide on boiling, mercuric sulphide being formed.

When an ethereal solution of triphenylmethylthiol is treated in the cold with an equimolecular proportion of sulphuryl chloride, *triphenylmethyl thiochloride* [*chlorothioltriphenylmethane*] is deposited in yellow prisms, m. p. 137° , according to the equation $\text{CPh}_3\cdot\text{SH} + \text{SO}_2\text{Cl}_2 = \text{CPh}_3\cdot\text{SCl} + \text{SO}_2 + \text{HCl}$. The compound is very stable towards water, but is decomposed by alkali hydroxides. The chlorine atom is readily replaced by other groups, using basic reagents, the following examples being described: (1) A solution of sodium methoxide gives *triphenylmethyl methoxyl sulphide*, $\text{CPh}_3\cdot\text{S}\cdot\text{OMe}$, needles, m. p. 124° , and sodium phenoxide forms *triphenylmethyl phenoxyl sulphide*, large prisms, m. p. $91\cdot5^{\circ}$. (2) Triphenylmethylthiol yields triphenylmethyl disulphide,



(*ibid.*). (3) Ammonia produces *triphenylmethyl sulphamide* [*triphenylmethylthiolamine*], $\text{CPh}_3\cdot\text{S}\cdot\text{NH}_2$, which crystallises in white rods, m. p. 126° , and forms an *acetyl* derivative, $\text{CPh}_3\cdot\text{S}\cdot\text{NHAc}$, needles, m. p. 187° , and a *benzylidene* compound, $\text{CPh}_3\cdot\text{S}\cdot\text{N}:\text{CHPh}$, yellow needles, m. p. 128° . (4) Methylamine yields *triphenylmethyl methylsulphamide* [*triphenylmethylthiolmethylamine*], leaflets, m. p. 119 — 120° , which forms an *acetyl* derivative, prismatic needles, m. p. 133° , and a *nitroso*-compound,

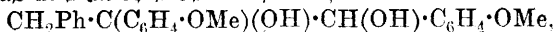


colourless crystals, m. p. 102 — 103° (decomp.). (5) Dimethylamine gives *triphenylmethylthiol dimethylamine*, m. p. 105 — 108° . (6) Aniline forms *triphenylmethyl phenylsulphamide* [*triphenylmethylthiolaniline*], white tablets, m. p. 103° , and *o*-toluidine gives *triphenylmethylthiol-o-toluidine*, leaflets, m. p. 141° .

If a solution of triphenylmethylthiol in benzene is shaken with sodium nitrite solution and gradually treated with dilute sulphuric acid, or slowly mixed with liquid nitrogen trioxide or peroxide, *triphenylmethyl thionitrite*, $\text{CPh}_3\cdot\text{S}\cdot\text{NO}$, separates in green needles, m. p. 104° (decomp.). Concentrated solutions of this ester in benzene appear red in transmitted light and green by reflected light. The thiol also couples with benzenediazonium chloride in the presence of sodium hydroxide, giving *triphenylmethylthiodiazobenzene*, $\text{CPh}_3\cdot\text{S}\cdot\text{N}_2\cdot\text{Ph}$, yellow leaflets, m. p. 108° (decomp.).

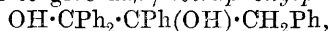
Chlorothioltrichloromethane (perchloromethyl mercaptan) condenses with benzene under the influence of aluminium chloride to form *thiobenzophenone*, $\text{Ph}\cdot\text{CS}$, a deep blue oil which yields benzophenone on boiling with alcoholic potassium hydroxide, and tetraphenylethylene on heating with copper powder. J. C. W.

Molecular Transpositions of the α -Glycols. V. The Dehydration of a Methoxy-derivative of $\alpha\beta$ -Triphenylpropane- $\alpha\beta$ -diol. A. ORÉKHOFF [with F. COMA Y ROCA] (*Bull. Soc. chim.*, 1919, [iv], 25, 174—179. Compare this vol., i, 205, 206).—Magnesium benzyl bromide condenses with *p*-anisoin to give *γ -phenyl- $\alpha\beta$ -di-*p*-anisylpropane- $\alpha\beta$ -diol*,



m. p. 152—153°, which when dehydrated with sulphuric acid yields *benzyl-di-p-anisylacetaldehyde*, $\text{CH}_2\text{Ph}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{OMe})_2\cdot\text{CHO}$, m. p. 71—72°, giving an *oxime*, m. p. 116—118°. The aldehyde is decomposed by alcoholic potassium hydroxide, yielding *α -phenyl- $\beta\beta$ -di-p-anisylethane*, m. p. 89—90°. The constitution of this latter compound was proved by its synthesis as follows: Di-*p*-anisyl ketone condenses with magnesium benzyl chloride, giving *phenyl-di-p-anisylethyl alcohol*, $\text{CH}_2\text{Ph}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{OMe})_2\cdot\text{OH}$, m. p. 141—142°, which when dehydrated by acetyl chloride yields *phenyl-di-p-anisylethylene*, $\text{CHPh}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{OMe})_2$, m. p. 62—63°, and this, when reduced by sodium in absolute alcohol, gives *α -phenyl- $\beta\beta$ -di-p-anisylethane*. W. G.

Molecular Transpositions of the α -Glycols. VI. Dehydration of $\alpha\alpha\beta\gamma$ -Tetraphenylpropane- $\alpha\beta$ -diol. A. ORÉKHOFF [with J. ZIVE] (*Bull. Soc. chim.*, 1919, [iv], **25**, 179—182. Compare preceding abstract).—Magnesium benzyl chloride condenses with phenylbenzoin to give *$\alpha\alpha\beta\gamma$ -tetraphenylpropane- $\alpha\beta$ -diol*,



m. p. 141—142°, which when dehydrated with sulphuric acid yields *benzyl triphenylmethyl ketone*, $\text{CPh}_3\cdot\text{CO}\cdot\text{CH}_2\text{Ph}$, m. p. 113—113·5°; this is decomposed by alcoholic potassium hydroxide, giving triphenylmethane and potassium phenylacetate. W. G.

Molecular Transpositions of the α -Glycols. VII. The Dehydration of $\alpha\beta$ -Diphenylbutane- $\alpha\beta$ -diol and of $\alpha\beta$ -Diphenylmethylpentane- $\alpha\beta$ -diol. A. ORÉKHOFF [with J. ZIVE] (*Bull. Soc. chim.*, 1919, [iv], **25**, 182—186. Compare preceding abstract).—By dehydrating $\alpha\beta$ -diphenylbutan- $\alpha\beta$ -diol with hot 20% sulphuric acid, Tiffeneau and Dorlencourt obtained *$\alpha\alpha$ -diphenylbutaldehyde* (compare A., 1906, i, 724). The authors, by using cold concentrated sulphuric acid, obtained ethyldeoxybenzoin and an *isomeride*, m. p. 32—33°, giving a *semicarbazone*, m. p. 191—192°, which was not characterised.

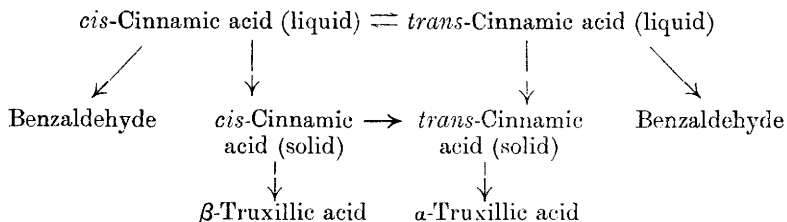
Magnesium *isobutyl* bromide condenses with benzoin to give *$\alpha\beta$ -diphenyl- δ -methylpentane- $\alpha\beta$ -diol*, m. p. 101—109°, which when dehydrated with cold concentrated sulphuric acid yields *isobutyldeoxybenzoin*. W. G.

Molecular Transpositions of the α -Glycols. VIII. The Constitution of the Product of Dehydration of $\alpha\beta\beta$ -Triphenylethanedil. A. ORÉKHOFF (*Bull. Soc. chim.*, 1919, [iv], **25**, 186—189).—The author agrees with Kohler (compare A., 1906, i, 753) that the product of dehydration of $\alpha\beta\beta$ -triphenylethanedil is diphenylacetophenone, $\text{CHPh}_2\cdot\text{COPh}$, and not the so-called triphenylvinyl alcohol, $\text{CPh}_2\cdot\text{CPh}\cdot\text{OH}$ (compare Biltz, A., 1899, i, 439). Diphenylacetophenone condenses with magnesium phenyl bromide to give *$\alpha\alpha\beta\beta$ -tetraphenylethyl alcohol*, m. p. 235—236°, which is also obtained by the action of magnesium phenyl bromide on diphenylacetyl chloride. The alcohol, when dehydrated, yields tetraphenylethylene.

Diphenylacetophenone condenses with magnesium benzyl chloride to give $\alpha\beta\gamma$ -tetraphenylpropan- β -ol, m. p. 135—136°. W. G.

Action of Light on *allo*- and *iso*-Cinnamic Acids. HANS STOBBE (*Ber.*, 1919, 52, [B], 666—672).—Two specimens of cinnamic acid, m. p. 42°, obtained from the acids, m. p.'s 68° and 58° respectively, were exposed to bright daylight during two years; the product consisted entirely of unchanged acid and β -truxillic acid.

[With JUSSIK POGOSIANZ.]—Specimens of cinnamic acids, m. p.'s 42°, 58°, and 68° respectively, were exposed in quartz tubes to direct sunlight which was sufficiently powerful in the circumstances to cause temporary fusion, with consequent isomerisation; in each case, the product consisted chiefly of α -truxillic acid with little β -truxillic acid and minimal quantities of *trans*-cinnamic acid and benzoic acid. Reaction in the illuminated molten mass, and also in benzene solution, may be represented by the scheme:



[With EDUARD FAERBER.]—The possible polymerisation of cinnamic acid by heat has been investigated either alone or in the presence of a solvent (water, naphthalene, xylene, ethylene dibromide). Polymerisation was only observed with certainty in the experiment with ethylene dibromide, when α -truxillic acid was formed in small amount. It is suggested that the action may be due to slight decomposition of the solvent into bromoethylene and hydrogen bromide, and the catalytic influence of the latter.

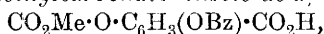
H. W.

The *O*-Benzoyl Derivatives of β -Resorcylic and Gentisic Acids. MAX BERGMANN and PAUL DANGSCHAT (*Ber.*, 1919, 52, [B], 371—388).—In a recent paper (*A.*, 1918, i, 172), Fischer described a remarkable reaction of the acyl derivatives of some aromatic acids containing at least two hydroxyl groups in neighbouring positions, namely, the wandering of an acyl group from one place to another during hydrolysis. For example, 4-benzoyl-3-acetylprotocatechuic acid yields 3-benzoylprotocatechuic acid. In order to prove whether this phenomenon is connected with the juxtaposition of the hydroxyl groups, Fischer has suggested the present investigation on β -resorcylic and gentisic acids, in which the hydroxyl groups are, respectively, in meta- and para-arrangement. The authors have succeeded in isolating the two pairs of

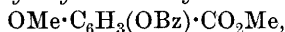
monobenzoates, but have found no indications of a tendency for the benzoyl group to wander from one position to the other.

Protocatechuic and gallic acids also only yield one carbomethoxy- or acetyl derivative, the acyl group being in the meta-position with respect to the carboxyl group. β -Resorcylic and gentisic acids yield *o*-acyloxy-compounds as well as meta- or para-derivatives.

2-Benzoyloxy-4-methylcarbonatobenzoic acid,



is obtained in long, thin needles, m. p. 148—149° (corr.), by the action of benzoyl chloride on carbomethoxyresorcylic acid (Fischer, A., 1909, i, 161), and is hydrolysed by means of *N*-ammonia solution to *4-hydroxy-2-benzoyloxybenzoic acid*, which crystallises in concentric groups of needles, m. p. 160—161° (corr.). When treated with an excess of diazomethane in dry acetone, this acid yields *methyl 2-benzoyloxy-4-methoxybenzoate*,



which crystallises in needles or flat prisms, m. p. 69—70°, and is hydrolysed by dilute aqueous-alcoholic sodium hydroxide to 4-methoxysalicylic acid, m. p. 161° (corr.) (compare Tiemann and Parrisius, A., 1881, 270). The last compound affords the clue to the constitution of the benzoyloxy-acids.

2:4-Diacetoxybenzoic acid, well-developed, microscopic prisms, m. p. 136—138°, is obtained by heating β -resorcylic acid with acetic anhydride and zinc chloride, and is partly hydrolysed by dilute sodium hydroxide at 0° to *4-hydroxy-2-acetoxybenzoic acid*, which crystallises in lanceolate leaflets, m. p. 167—168° (corr.). This acid yields *methyl 2-acetoxy-4-methoxybenzoate*, m. p. 56—57°, on treatment with diazomethane, and this ester may be hydrolysed to 4-methoxysalicylic acid. The acid also gives *4-benzoyloxy-2-acetoxybenzoic acid*, flat needles or prisms, m. p. 148—149° (corr.), when treated with benzoyl chloride and pyridine, and this is partly hydrolysed by a mixture of acetic and hydrochloric acids to *2-hydroxy-4-benzoyloxybenzoic acid*, needles, m. p. 193—194° (corr.). Treatment with diazomethane gives *methyl 4-benzoyloxy-2-methoxybenzoate*, m. p. 78—80°, which is hydrolysed by dilute aqueous-alcoholic sodium hydroxide to Fischer and Pfeffer's 4-hydroxy-2-methoxybenzoic acid, decomp. 187—189° (corr.) (A., 1912, i, 559).

2-Benzoyloxy-5-methylcarbonatobenzoic acid, long, flat needles, m. p. 148—149° (corr.), is obtained from carbomethoxygentisic acid (A., 1909, i, 161) and hydrolysed by *N*-ammonia solution to *5-hydroxy-2-benzoyloxybenzoic acid*, which crystallises in microscopic leaflets, m. p. 211—212° (corr.). When treated with diazomethane, this yields *methyl 2-benzoyloxy-5-methoxybenzoic acid*, stout, quadratic plates, m. p. 106—107° (corr.), which gives the known 5-methoxysalicylic acid, m. p. 145—146° (corr.), on hydrolysis (Tiemann and Müller, A., 1882, 52). A characteristic difference between this acid and the isomeric 5-hydroxy-2-methoxybenzoic acid, m. p. 155—156° (Fischer and Pfeffer, *loc. cit.*), is that the

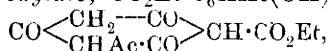
former gives a deep blue colour with ferric chloride and the latter only a grey colour.

5-Hydroxy-2-acetoxybenzoic acid, twinned prisms, m. p. 171—173° (corr.), is obtained by the partial hydrolysis of diacetyl-gentisic acid (Hemmelmeyer, A., 1909, i, 387) with *N*-ammonia in an atmosphere of hydrogen, and is converted by diazomethane into *methyl 2-acetoxy-5-methoxybenzoate*, m. p. 45—46°, which is hydrolysed to the above 5-methoxysalicylic acid. It is also converted into *5-benzoyloxy-2-acetoxybenzoic acid*, which crystallises in microscopic, bent needles, m. p. 166—167° (corr.), and yields *2-hydroxy-5-benzoyloxybenzoic acid*, leaflets, m. p. 178—179° (corr.), on hydrolysis with a mixture of acetic and hydrochloric acids. When treated with diazomethane, the acid gives *methyl 5-benzoyloxy-2-methoxybenzoate*, m. p. 83—84°, which may be hydrolysed to 5-hydroxy-2-methoxybenzoic acid. J. C. W.

Guaiaretic Acid. J. HERZIG and F. SCHIFF (*Ber.*, 1919, **52**, [B], 260).—The authors agree with Schroeter and others (this vol., i, 84) that the formula of guaiaretic acid is $C_{20}H_{24}O_4$. J. C. W.

Some Derivatives of Phloroglucinol. ADOLF SONN (*Ber.*, 1919, **52**, [B], 255—259).—Mosimann and Tambor have found that acetophloroglucinol will not condense with *p*-hydroxybenzaldehyde (A., 1916, i, 822), whereas its di- and tri-methyl ethers condense readily, and Sonn has found the same indifference in the case of ethyl acetophloroglucinolcarboxylate. This is most probably due to the fact that the compounds are really derivatives of triketohexamethylene.

The above ester is obtained by boiling a solution of Jerdan's lactone (A., 1917, i, 277; 1918, i, 33) in a mixture of acetic and hydrochloric acids, carbon dioxide being evolved. *Ethyl 2-acetylphloroglucinol-4-carboxylate*, $CO_2Et \cdot C_6HAc(OH)_3$ or



crystallises in bundles of slender needles, m. p. 77—78°, and changes into *ethyl phloroglucinolcarboxylate* when left with 25% potassium hydroxide. This ester crystallises from water with $1H_2O$, or from alcohol in anhydrous prisms or needles, m. p. 129°.

When Jerdan's lactone is left for some time with 33% potassium hydroxide and the solution is acidified, *ethyl ω -carboxyphloroacetophenonecarboxylate* [*3-carbethoxyphloroacetophenoneacetic acid*], $CO_2Et \cdot C_6H(OH)_3 \cdot CO \cdot CH_2 \cdot CO_2H$, is precipitated. The acid has m. p. 160°, and changes into the above ethyl 2-acetylphloroglucinol-4-carboxylate on melting or warming with acetic anhydride.

The silver salt of Jerdan's lactone, when heated with ethyl iodide, yields *ethyl 5:7-dihydroxy-4-ethoxy-1:2-benzopyrone-6(or 8)-carboxylate*, $CO_2Et \cdot C_6H(OH)_2 \begin{array}{c} O \text{---} CO \\ C(OEt) \cdot CH \end{array}$, in thin, prismatic crystals, m. p. 160°. J. C. W.

Constitution of Bile Acids. I. Cholanic, *iso*Cholanic, and ψ -Cholanic Acids. W. BORSCHKE and EMMY ROSENKRANZ (*Ber.*, 1919, **52**, [B], 342—345).—When bilianic and *isobilianic* acids, $C_{19}H_{31}(CO)_2(CO_2H)_3$, are reduced by means of amalgamated zinc and hydrochloric acid, they yield cholanic and *isocholanic* acids, $C_{20}H_{33}(CO)(CO_2H)_3$. The ketone group of the latter pair of isomerides therefore corresponds in position with one ketone group of the former pair, and accordingly the $-CH\cdot OH-$ groups of deoxycholic acid and cholic acid which gave rise to these ketonic acids are identically placed. It has already been proved that the second alcoholic group of deoxycholic acid, $C_{24}H_{40}O_4$, is identical with a second group in cholic acid, $C_{24}H_{40}O_5$, the evidence being the great similarity between the ketonic tricarboxylic acids, namely, the pairs of bilianic and cholanic acids, which these hydroxy-acids yield on oxidation with permanganate. Consequently, cholic acid is a hydroxydeoxycholic acid.

When deoxycholic acid is oxidised by chromic acid, it yields dehydrodeoxycholic acid, $C_{21}H_{35}(CO)_2\cdot CO_2H$, and when this is oxidised by alkaline permanganate it gives ψ -cholanic acid, m. p. 259—260° (decomp.). This is another isomeride of cholanic acid, $CO\cdot C_{20}H_{33}(CO_2H)_3$, the constitution of which will be investigated more fully.

J. C. W.

Improved Preparation of Aromatic Aldehydes. GUSTAVE BLANC (*Eng. Pat.*, 115244).—Aromatic aldehydes free from any trace of carboxylic acid are produced by boiling aromatic chloromethylene derivatives with an aqueous solution of an alkali dichromate, preferably with the addition of an alkali hydroxide or carbonate. The reaction is approximately represented by the equation $3R\cdot CH_2Cl + Cr_2O_7Na_2 + NaOH = 3NaCl + 3R\cdot CHO + Cr_2O_3 + 2H_2O$. [See, further, *J. Soc. Chem. Ind.*, 1919, June.]

G. F. M.

Terpenes and Ethereal Oils. CXXXVI. O. WALLACH (*Annalen*, 1919, **418**, 36—69).—I. *Conversion of Menthone into Pulegenone* [with EMMA GROTE].—This work has already been recorded (*A.*, 1918, i, 544).

II. *Eucarvone Series* [with MAX STAUDACHER].—The experiments on the behaviour of halogenated cyclic ketones towards aqueous alkali (*A.*, 1918, i, 440, 442, 444) have been extended to include members of the eucarvone series. β -Dihydroeucarvone (*Annalen*, 1914, **403**, 91), the constitution of which has not yet been ascertained, is smoothly converted by bromine (1 mol.) in cold glacial acetic acid solution into a *dibromide*, $C_{10}H_{16}OBr_2$, prisms, m. p. 71—72°, which is isomeric with the dibromide, m. p. 68°, obtained by the bromination of tetrahydroeucarvone (*A.*, 1918, i, 444). The new dibromide, m. p. 71—72°, reacts rapidly with warm 2% aqueous potassium hydroxide, yielding volatile products and an *acid*, $C_{10}H_{16}O_2$. The volatile products have not been obtained in sufficient quantity for complete examination, but they consist chiefly of a ketone which shows no similarity to ketones of the

eucarvone series. It readily forms a *semicarbazone* (? $C_{11}H_{19}O_2N_3$ or $C_9H_{17}ON_3$), crystals, m. p. 194—195°, has an odour of camphor, behaves towards permanganate as an unsaturated compound, and by reduction with hydrogen and palladium yields a saturated ketone (*semicarbazone*, m. p. 196—197°).

The acid, $C_{10}H_{16}O_2$, is shown by direct comparison to be identical with Tiemann and Semmler's α -*cyclogeranic* (*isogeranic*) acid, m. p. 104—105°. Consequently, the dibromide, m. p. 71—72°, probably has the formula $\begin{matrix} CMe_2 \cdot CH_2 \cdot CO \\ CH_2 \cdot CH_2 \cdot CHBr \end{matrix} > CMeBr$, and β -dihydroeucarvone has the 7-ring formula originally suggested (*loc. cit.*).

Since the dibromide contains a methylene group adjacent to a carbonyl group, it ought, according to previous experience of the bromination of cyclic ketones (*loc. cit.*), to undergo direct bromination. This is so. By treatment with bromine (1 mol.) in almost boiling glacial acetic acid, it yields a *tribromide*, $C_{10}H_{15}OBr_3$, m. p. 104—105°, which is only slowly attacked by 2% potassium hydroxide at 70°, yielding an *acid*, m. p. about 170°. The isomeric dibromide, m. p. 68°, obtained from tetrahydroeucarvone, does not undergo further bromination under the above conditions. The volatile products obtained when it is shaken with 2% alkali solution (*loc. cit.*) contain a small quantity of a hydrocarbon (?), b. p. 138—140°, and a yellow substance, b. p. 93—95°/8 mm., D^{20}_D 0.988, n^{20}_D 1.4813 (these values are only given provisionally), which does not yield any characteristic derivatives, but is converted by reduction with hydrogen and palladium into a *substance*, b. p. 223—225°, D^{20}_D 0.9690, n^{20}_D 1.4690 (*semicarbazone*, $C_{11}H_{21}ON_3$, m. p. 212—213°; *oxime*, m. p. 55—56°), which is probably a cyclic ketone having its oxygen atom in a side-chain.

The acid, $C_{10}H_{16}O_2$, m. p. 91.5—92.5°, obtained by the action of 2% potassium hydroxide on dibromotetrahydroeucarvone (*loc. cit.*), is converted by oxidation with alkaline permanganate into a mixture of three acids, $C_{10}H_{16}O_3$, m. p. 159—160°, $C_{10}H_{14}O_3$, m. p. 187°, the third acid, m. p. 90—91°, being produced in very small quantity.

Since the preceding brominated 7-ring ketones of the eucarvone series differ from halogenated 6-ring ketones in yielding volatile products as well as an acid by treatment with 2% potassium hydroxide, *dibromosuberone*, $C_7H_{10}OBr_2$, m. p. 70—72°, has been shaken with dilute potassium hydroxide solution at 70°, whereby a volatile ketone (*semicarbazone*, m. p. 190—191°) and an acid, probably tetrahydrobenzoic acid, have been obtained. C. S.

Adsorption of the Glucosides of Digitalis Leaves. C. MANNICH (*Ber. Deut. pharm. Ges.*, 1919, **29**, 206—213).—Experiments with gitalin showed the latter to be readily adsorbed from aqueous solution by blood charcoal (the latter can adsorb at least 20% of its weight), less readily from alcoholic solution, and still less readily from solution in chloroform. A specimen of charcoal containing 20% of gitalin did not lose glucoside when treated with

water, and only a portion when alcohol was used, but practically all of it was removed by chloroform. Other substances, such as fuller's earth, the sulphides of lead, copper, or zinc, and particularly those of arsenic and antimony, have the power of adsorbing the bitter principles from an aqueous extract of digitalis leaves. Attempts to isolate the glucosides by treatment of infusion of digitalis with animal charcoal and subsequent extraction of the latter with chloroform did not lead to the desired result, possibly because the principles are not free in the aqueous solution, but in complex compounds with other substances, such as tannins.

The author considers that the readiness with which the digitalis glucosides are adsorbed by the powdered drug explains the difficulty of their complete extraction, and also the better results which are obtained when water, as solvent, is replaced by alcohol. H. W.

Syntheses of Depsides, Lichen Substances, and Tannins.

II. EMIL FISCHER (*Ber.*, 1919, **52**, [B], 809—829).—A general résumé of the progress made by Fischer and his co-workers in this field since the year 1913; the individual subjects have been previously abstracted. H. W.

Tannin and the Synthesis of Similar Substances. VI.

EMIL FISCHER and MAX BERGMANN (*Ber.*, 1919, **52**, [B], 829—854. Compare A., 1912, i, 471, 887; 1913, i, 479; 1915, i, 437; 1918, i, 87).—The removal of acetyl groups from substances such as the acetates of galloyl- and digalloyl-glucose, previously effected with cold alkali or with warm sodium acetate solution, can also be effected at the ordinary temperature by a moderate amount of concentrated aqueous hydrochloric acid in methyl-alcoholic solution. If the acetyl derivative is too sparingly soluble in methyl alcohol, a mixture of the latter with acetone may be used. The penta(*m*-digalloyl)- α - and - β -glucoses obtained in this manner from the acetates are optically purer than those previously obtained. The method can also be applied with good results to simpler substances, such as acetylsalicylic acid and triacetyl gallic acid.

The use of the potassium salt for the purification of tannins was recommended by Berzelius. The authors find the most convenient method of preparation to consist in mixing alcoholic solutions of the natural or synthetic tannins and potassium acetate, but the precipitates contain small quantities of the latter. The salts from Chinese tannin, pentadigalloyl- α -glucose, pentadigalloyl- β -glucose, and pentagalloyl glucose have $[\alpha]_D +46.3^\circ$, $+56.6^\circ$, and $+33.7^\circ$, respectively, in water. The salt appears to be suitable for the separation of artificial tannins from many other substances and for their purification, but not suitable for the differentiation of the individual galloyl glucoses.

Attempts have been made to extend the method used in the preparation of 1-monogalloyl- β -glucose (this vol., i, 89) to other 1-acylglucoses, but the results are disappointing, as frequently the acyl group is removed simultaneously with the acetyl groups. This

is, for example, the case with 1-*benzoyltetra-acetyl- α -glucose*, long, colourless needles, m. p. 60—63°, but frequently several degrees lower, owing possibly to dimorphism, $[\alpha]_D^{25} + 113.5^\circ$ in chloroform. On the other hand, 1-*p-acetoxybenzoyltetra-acetyl- β -glucose*, colourless needles, m. p. 172—173° (corr.), $[\alpha]_D - 30.6^\circ$ in *s*-tetrachloroethane, could be converted by alcoholic sodium hydroxide or alcoholic ammonia into 1-*p-hydroxybenzoyl- β -glucose*, flat needles, m. p. about 228° (corr.; decomp.) when rapidly heated, $[\alpha]_D^{25} - 23.9^\circ$ in *s*-tetrachloroethane; in the latter case, 1-*p-hydroxybenzoyltetra-acetyl- β -glucose*, m. p. 196—197° (corr.), $[\alpha]_D^{25} - 38.4^\circ$ in acetone, is formed as intermediate product. Similarly, 1-*p-acetoxybenzoyltetra-acetyl- α -glucose*, m. p. 134—135° (corr.), $[\alpha]_D + 116^\circ$ in *s*-tetrachloroethane, could be de-acetylated with alcoholic sodium hydroxide, but the product was a syrup which could not be caused to crystallise or reconverted into the pure penta-acetate.

The catalytic action of sodium alkoxide on esters in alcoholic solution has been applied for the removal of acetyl groups. Thus, for the elimination of the five acetyl groups of *p*-acetoxybenzoyltetra-acetylglucose dissolved in alcohol, one molecule of sodium ethoxide is sufficient at the ordinary temperature, and the presence of a small quantity of water in the alcohol does not hinder the reaction; these conditions are particularly advantageous for securing good yields. The method has also been applied to the isolation of dextrose from its penta-acetate and of α -methylglucoside from its tetra-acetate.

Attempts to prepare 1-galloyl- α -glucose are described. It is found that the specific rotation of 1-galloyl- β -glucose gradually changes from negative to positive, and finally attains a maximum when its aqueous solution is agitated with calcium carbonate, or, more rapidly, with sodium carbonate or pyridine; in all probability, the change in sign is caused by the conversion of 1-galloyl- β -glucose into the α -derivative, but attempts to isolate the latter from the product were not successful. Crude tetra-acetyl- α -glucose, obtained by inversion of the β -compound, was therefore treated with triacetylalloyl chloride in the presence of quinoline, whereby ultimately *triacetylalloyltetra-acetyl- α -glucose*, microscopic needles, m. p. 158—159° (corr.), $[\alpha]_D^{25} + 99.9^\circ$ in *s*-tetrachloroethane, was isolated; this was then hydrolysed with alcoholic ammonia, but the product was not crystalline. It appeared, however, to contain considerable amounts of 1-galloyl- α -glucose, since, on re-acetylation, it yielded the hepta-acetyl derivative in quantity.

The galloyl derivatives of the sugars differ among themselves in their behaviour towards gelatin solutions. The penta- and tri-galloyl compounds precipitate the latter from aqueous solution in the same manner as do the tannins, but this property is not shown by the varying monogalloyl glucoses nor by monogalloyl fructose. Since similar differences were to be expected among the polyhydroxy-alcohols, the derivatives of glycol, trimethyleneglycol, glycerol, erythritol, and mannitol have been prepared and ex-

aminated. They are readily obtained from the alcohols by coupling with triacetylalloyl chloride and subsequent removal of the acetyl groups. The crystalline *ethyleneglycol digallate* is so sparingly soluble in water or alcohol that its reaction with gelatin and arsenic acid cannot be investigated. With *trimethyleneglycol digallate*, the gelatin test is not characteristic, but distinct gelatinisation is caused by arsenic acid in alcoholic solution. *Erythritol tetragallate* is readily soluble in water and coagulates gelatin, but the alcoholic solution is too dilute to be tested with arsenic acid. The amorphous *glyceryl trigallate* and *mannitol hexagallate* yield colloidal solutions in water and behave like tannins towards both reagents. The physical properties of this series of substances are as follows: *ethyleneglycol ditriacetyl-gallate*, colourless leaflets, m. p. 172—173° (corr.) after slight softening; *ethyleneglycol digallate*, microscopic needles, which decompose at about 287° (corr.) without melting; *glyceryl tri-triacetyl-gallate*, amorphous powder; *glyceryl trigallate*, pale yellow, amorphous, brittle mass. [With (FRL.) HERTHA VON PELCHERZIM.]—*Trimethyleneglycol ditriacetyl-gallate*, leaflets, m. p. 159—160°; *trimethyleneglycol digallate*, leaflets, m. p. about 270° (decomp.); *erythritol tetra-triacetyl-gallate*, small, colourless needles without definite m. p.; *erythritol tetragallate*, which when rapidly heated darkens at about 288°, and is completely decomposed at about 308°; *mannitol hexa-triacetyl-gallate*, amorphous, pale brown substance; *mannitol hexagallate*, amorphous, pale brown substance, $[\alpha]_D^{18} + 27.0^\circ$ in alcohol.

H. W.

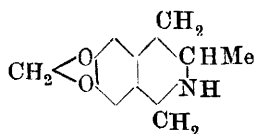
The Resolution of Hyoscine and its Components, Tropic Acid and Oscine. HAROLD KING (T., 1919, 115, 476—508).

A New Synthesis of Hydrastinine and its Homologues. KARL W. ROSENMUND (*Ber. Deut. pharm. Ges.*, 1919, 29, 200—206).—Starting from methylenedioxyphenylisopropylamine, the synthesis of certain homologues of hydrastinine has been effected, whilst the alkaloid itself has been prepared from homopiperonylamine by a new method.

Methylenedioxyphenylisopropylaminomethanol,



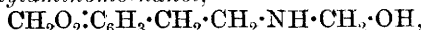
is obtained as a viscous, colourless, somewhat unstable oil by the action of chloromethyl alcohol on methylenedioxyphenylisopropylamine in dry ethereal solution, and is converted by warming with 10% aqueous hydrochloric acid into 3-methyldihydronorhydrastinine hydrochloride, m. p. 231—232°; the free base (annexed formula) crystallises in colourless leaflets, m. p. 57—58°; the *hydriodide* forms colourless leaflets, m. p. 215—217°. Methylation of the base, preferably with formaldehyde, gives 3-methyldihydrohydrastinine, m. p. 85—87° (*hydrochloride*, m. p. 230—232°; *hydriodide*, m. p. 240°; *perchlorate*, colour-



less needles, m. p. 215°), which can also be prepared from methylenedioxyphenylisopropylmethylamine. Oxidation with potassium dichromate and sulphuric acid or with iodine leads to the formation of 3-methylhydrastinine, m. p. $107-108^{\circ}$ (hydriodide, yellow leaflets, m. p. $210-212^{\circ}$; perchlorate, greenish-yellow needles, m. p. 212°).

Phenylacetylmethylenedioxyphenylisopropylamine, colourless needles, m. p. $105-106^{\circ}$, is prepared by the action of phenylacetyl chloride on the amine, and is converted by treatment with phosphoric oxide into 1-benzyl-3-methylnorhydrastinine, yellow syrup (picrate, m. p. 182° ; hydriodide, shining prisms, m. p. 208°).

Homopiperonylaminomethanol,



is obtained as a colourless, very unstable oil by the action of chloromethyl alcohol (1 mol.) on homopiperonylamine (2 mols.) in ethereal solution, and is converted by 10% aqueous hydrochloric acid into dihydronorhydrastinine, identical with the product described by Decker (A., 1911, i, 906). H. W.

Porphyroxine. JITENDRA NATH RAKSHIT (I., 1919, 115, 455-461).

Syntheses in the Indole Series. Homologues of Di-oxindole and Isatin. J. MARTINET (Ann. Chim., 1919, [ix], 11, 15-84, 85-130).—For the most part a more detailed account of work already published (compare A., 1913, i, 756; 1918, i, 306, 345, 351). The following new compounds are described.

Methyl diacetyl-5-methyldioxindole-3-carboxylate, m. p. 132° , and the corresponding ethyl ester, m. p. 110° .

Methyl 5:7-dimethyldioxindole-3-carboxylate, m. p. 260° , and its diacetyl derivative, m. p. 227° ; the corresponding ethyl ester, m. p. 215° , and its diacetyl derivative, m. p. $203-204^{\circ}$; 5:7-dimethyldioxindole, m. p. $228-229^{\circ}$, and its O-acetyl derivative, m. p. $201-202^{\circ}$.

Methyl acetyl-1-methyldioxindole-3-carboxylate, m. p. 146° , and the ethyl ester, m. p. 65° .

Ethyl 5-bromo-1-methyldioxindole-3-carboxylate, m. p. 160° , and its acetyl derivative, m. p. 132° ; 5-bromo-1-methyldioxindole, m. p. 162° , and its O-acetyl derivative, m. p. 115° ; 5-bromo-1-methylisatinphenylhydrazone, m. p. 164° .

Ethyl acetyl-1-ethyldioxindole-3-carboxylate, m. p. 68° .

Ethyl 5-bromo-1-ethyldioxindole-3-carboxylate, m. p. 106° , and its acetyl derivative, m. p. 120° ; 5-bromo-1-ethylisatin, m. p. 144° , and its phenylhydrazone, m. p. 124° .

Methyl 3-hydroxy-2-keto-1-ethyldihydro- $\beta\beta$ -naphthindole-3-carboxylate, m. p. 203° , and its acetyl derivative, m. p. 140° , and the acetyl derivative, m. p. 114° , of the corresponding ethyl ester.

Ethyl 3-acetyl-1:7-trimethylenedioxyindole-3-carboxylate, m. p. 95° .

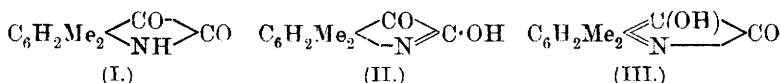
5-Methyl-1:7-trimethylenedioindole, m. p. 193°; 5-methylisatinphenylhydrazone, m. p. 268°; 1-ethylisatinphenylhydrazone, m. p. 74°; N-ethyl-β-naphthisatinphenylhydrazone, m. p. 180°.

β-Naphthisatoic acid (β-amino-α-naphthylglyoxylic acid) is very unstable, but gives potassium, copper, lead, and silver salts.

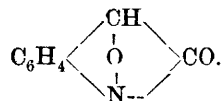
5-Bromo-N-methylisatoic acid (5-bromo-2-methylaminophenylglyoxylic acid) is very unstable, but gives potassium, copper, silver, and lead salts; 5-bromo-N-ethylisatoic acid also gives potassium, copper, silver, and lead salts.

N-Ethyl-β-naphthisatoic acid (β-ethylamino-α-naphthylglyoxylic acid) gives potassium, copper, and lead salts. W. G.

New Isomerides in the Isatin Series. III. GUSTAV HELLER (*Ber.*, 1919, **52**, [B]. 437—446. Compare A., 1917, i, 219; 1918, i, 235; this vol., i, 36).—The constitutions of three of the four modifications of 5:7-dimethylisatin have already been established, and the following formulæ assigned to them:



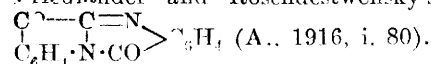
In the case of isatin itself, only the isomerides corresponding with these three formulæ have been established so far, but it is now found that when the methyl ether of the lactim form (II) of isatin is heated with benzene at 200—205°, it is partly converted into the N-methyl ether of the lactam form (I) and partly demethylated and transformed into a new isomeride which corresponds with the fourth modification of dimethylisatin. This is a feeble base the salts of which are hydrolysed by water. It does not react with diazomethane, methyl iodide, sodium hydrogen sulphite, or Fehling's solution, neither does it form an acetyl or benzoyl derivative nor give the indophenine reaction. It is more soluble in benzene than the other product, and its properties are best expressed in the annexed formula. The compound is designated *isatinone*, and it crystallises in well-developed, dark honey-coloured, quadratic prisms, m. p. 226° (decomp.). It dissolves slowly in 0.5N-sodium hydroxide, and if the solution is quickly precipitated by



50% acetic acid, a fifth isomeride, *isatinol* (annexed formula), is obtained in orange-yellow flocks, m. p. 255°, which reverts to isatinone on crystallisation from glacial acetic acid or benzene. The methyl ether of the fourth modification of dimethylisatin should conform to the same type. If the red solution in sodium hydroxide is exposed to light, however, it becomes pale in time and deposits



Friedländer and Roschdestwensky's anhydro-α-isatinanthranilide.



If the methyl ether of the lactim form of isatin is heated with methyl alcohol at 200° instead of with benzene, it yields this anhydro- α -isatinanthranilide and a *hydrate* of it, $C_{15}H_{10}O_3N_2$, colourless crystals, m. p. 172° , which yields anthranoylanthranilic acid when boiled with alcoholic potassium hydroxide.

J. C. W.

An Improved Method of Preparing Indican from Indigo-yielding Plants. BHAILAL M. AMIN (*Agric. Res. Inst. Pusa, Indigo Publ. No. 5*).—The method, which is far more rapid than any of the methods hitherto described, consists in extracting the fresh leaf with hot water so as to dissolve the indican. Freshly slaked lime is added to the extract to precipitate impurities, such as amino-acids, tannins, gums, etc. The purified liquor is filtered, evaporated, and the indican extracted from the concentrated solution with acetone. The wet extract is evaporated to remove the acetone, and on cooling in ice the aqueous solution which is left, indican hydrate separates. The crude hydrate is purified by dissolving it in absolute alcohol and precipitating with benzene, when pure anhydrous indican crystallises. This method gives an excellent yield (70–80%), and can be applied to any species of plant, and by its use pure indican has, for the first time, been prepared in large quantities from Java indigo (*Indigofera arrecta*).

W. G.

New Transitions from the Indole to the Quinoline Series. GUSTAV HELLER (*Ber.*, 1919, **52**, [B], 741–745).—It has been previously shown (Heller and Wunderlich, A., 1914, i, 865) that 2-cyano-2:3-dihydroindole-2-carboxylamide is converted by nitrous fumes into 2-hydroxyquinoline-3-carboxylamide. A similar conversion of the 5-membered to the 6-membered ring occurs when diazomethane acts on an ethereal suspension of isatin, 2:3-dihydroxyquinoline, needles, m. p. 190 – 192° , being obtained (compare Madelung, A., 1913, i, 91). The latter, with more diazomethane, appears to yield a monomethyl ether; with acetic anhydride, it gives a monoacetyl derivative, long needles, m. p. 214 – 215° .

Under similar conditions, *dihydroxy-6:8-dimethylquinoline*, m. p. about 242° (decomp.), is obtained from 2:4-dimethylisatin lactam, whilst 2:4-dimethylisatin lactim yields a *product*, aggregates of needles, m. p. 253° (decomp.).

Dimethylisatol and dimethylisatinone are normally alkylated by diazomethane, yielding, however, different substances, which are insoluble in alkali. Oxindole, dioxindole, and phthalimidine are not attacked by ethereal solutions of diazomethane.

H. W.

Action of Organomagnesium Compounds on Quinoline Methiodide. Stereochemistry of Compounds of Nitrogen.

MARTIN FREUND and ELISABETH KESSLER (*J. pr. Chem.*, 1918, [ii], **98**, 233–254. Compare A., 1905, i, 156; 1909, i, 417).—The action of magnesium propyl bromide on quinoline

methiodide yields 1-methyl-2-propyldihydroquinoline, $C_{13}H_{17}N$, as a golden-yellow, unstable oil, b. p. $268-270^{\circ}$ (compare von Braun and Aust, A., 1915, i, 586); the *picrate* forms needles, m. p. $157-158^{\circ}$. The base combines with methyl iodide, yielding a crystalline *methiodide*, m. p. $158-160^{\circ}$ (decomp.), which is converted at its melting point or by crystallisation from dilute alcohol into a compound, $C_{13}H_{16}NI$, m. p. 184° , which is identified as 2-propylquinoline methiodide. 1 : 2-Dimethyl-1 : 2-dihydroquinoline *methiodide*, yellowish-red crystals, m. p. $212-213^{\circ}$, does not exhibit similar behaviour. The dihydro-base does not yield crystalline salts; it combines with bromine, yielding a *perbromide*, $C_{13}H_{17}NBr_4$, needles, m. p. 158° , which, when treated with sulphurous acid and subsequently with sodium iodide, gives 3(4)-bromo-1-methyl-2-propyl-1 : 2-dihydroquinoline *hydriodide*, a yellow, crystalline salt, m. p. 242° , after darkening at 235° . The base is reduced by tin and hydrochloric acid to 1-methyl-2-propyltetrahydroquinoline, b. p. $270-280^{\circ}$ (compare von Braun and Aust, *loc. cit.*), which, when obtained in this manner, appears to be a mixture of two bases, one of which has b. p. $274-278^{\circ}$ and forms a crystalline *hydrochloride*, long needles, m. p. $237-238^{\circ}$, *hydrobromide*, needles, m. p. $223-224^{\circ}$, and *hydriodide*, m. p. 176° after softening at 168° , but does not give a crystalline methiodide, whilst the other, b. p. $272-276^{\circ}$, does not yield crystalline salts, but forms a crystalline *methiodide*, colourless leaflets, m. p. $196-197^{\circ}$ after some decomposition at 190° .

The action of magnesium *isobutyl* iodide on quinoline methiodide has been similarly studied with the object of discovering further instances of stereoisomerism of similar character. 1-Methyl-2-isobutyldihydroquinoline forms an unstable oil, b. p. $278-280^{\circ}$ (*picrate*, shining needles, m. p. $154-155^{\circ}$; the *methiodide* is not crystalline), which, as in the case of the propyl compound, is reduced to a mixture of bases, b. p. $260-280^{\circ}$, separable by means of their hydrochlorides. The one of these is a pale yellow, almost odourless oil, b. p. 283° (*hydrochloride*, transparent needles, m. p. $223-224^{\circ}$; *hydrobromide*, m. p. 225° after previous softening; *hydriodide*, m. p. $183-184^{\circ}$; *methiodide*, m. p. 168°), whilst the other is darker in colour, less pleasant in odour, has b. p. 263° , forms readily soluble salts with the halogen acids, and gives a *methiodide*, m. p. 174° after previous softening.

1-Methyl-2-isopropyldihydroquinoline is a yellow, unstable oil, b. p. $268-274^{\circ}$ (*picrate*, needles, m. p. 184°); it is reduced by tin and hydrochloric acid to 1-methyl-2-isopryltetrahydroquinoline, b. p. $265-266^{\circ}$. In this instance, the separation of possible isomerides could not be effected by means of halogen acids, owing to the solubility of the salts formed. Probably a mixture of stereoisomerides is present, since the crystalline *methiodide* (yellow needles, m. p. $179-180^{\circ}$) isolated from the crude base does not correspond in quantity with the weight of base used.

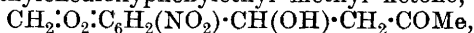
2-Benzyl-1-methyldihydroquinoline is obtained in poor yield by

the action of magnesium benzyl chloride on quinoline methiodide; the crude product is separable into two fractions, b. p. 125—140°/13—20 mm. and 140—155°/13—20 mm. respectively.

3-Bromo-2-phenyl-1-methyldihydroquinoline, b. p. 270°/75 mm., forms a brown, feebly basic oil, which has only a slight tendency towards salt formation; the *picrate* crystallises in four-sided leaflets, m. p. 185° after softening at 175°. H. W.

Some Derivatives of 6:7-Dihydroxyquinoline. W. BORSCHÉ and R. QUAST (*Ber.*, 1919, **52**, [B], 432—437).—A good method for the preparation of Haber's 6:7-methylenedioxy-2-methylquinoline is described (compare A., 1891, 705).

Piperonaldehyde is nitrated, and the 6-nitro-derivative, which is formed in good yield, is condensed with acetone in the presence of 3% potassium carbonate, whereby a 75% yield of β -hydroxy- β -6-nitro-3:4-methylenedioxyphenylethyl methyl ketone,



is obtained (compare Herz, A., 1905, i, 778). This is reduced by means of zinc dust in a mixture of acetic and hydrochloric acids, an excellent yield of 6:7-methylenedioxy-2-methylquinoline being obtained. The base has m. p. 150°, b. p. 306—308°/743 mm., and forms a *methiodide*, m. p. 277—278°, and a *methochloride*, m. p. 265—266°, which gives a *double salt* with mercuric chloride, m. p. 193° (decomp.). It condenses with benzaldehyde under the influence of zinc chloride to form 2-styryl-6:7-methylenedioxyquinoline, m. p. 179—180°, and it suffers reduction by sodium and alcohol to 6:7-methylenedioxy-2-methyl-1:2:3:4-tetrahydroquinoline, $\text{CH}_2:\text{O}_2:\text{C}_6\text{H}_2\begin{smallmatrix} \text{CH}_2\cdot\text{CH}_2 \\ \text{NH}\cdot\text{CHMe} \end{smallmatrix}$. This is a snow-white base,

m. p. 44—45°, which forms a *nitroso-compound*, yellow needles, m. p. 85—86°, and a *methiodide*, m. p. 176—177°.

The corresponding phenylquinoline has also been prepared. Piperonylideneacetophenone is nitrated, and the *phenyl 2-nitro-4:5-methylenedioxy-styryl ketone* so formed, which crystallises in flat, yellow needles, m. p. 165—166°, is reduced by zinc dust and a mixture of acetic and hydrochloric acids. 6:7-Methylenedioxy-2-phenylquinoline, $\text{CH}_2:\text{O}_2:\text{C}_6\text{H}_2\begin{smallmatrix} \text{CH}\cdot\text{CH} \\ \text{N}=\text{CPh} \end{smallmatrix}$, crystallises in very pale yellow leaflets, m. p. 110°, and its *picrate* has m. p. 192°.

J. C. W.

ψ -1:8-*iso*Naphthoxazones. BIMAN BIHARI DEY and MAHENDRA NATH GOSWAMI (*T.*, 1919, **115**, 531—541).

The Asymmetric Nitrogen Atom. LI. Abnormal Quaternary Ammonium Salts. E. WEDEKIND and TH. GOOST (*Ber.*, 1919, **52**, [B], 446—459).—In the last communication (A., 1916, i, 671), a diquaternary ammonium salt was described having two asymmetric nitrogen atoms of unlike asymmetry, namely, the

n*

salt of the formula $\text{NMePh}(\text{C}_7\text{H}_7)\text{Br}\cdot\text{C}_3\text{H}_6\cdot\text{NMePh}(\text{C}_3\text{H}_5)\text{I}$. With the hope of obtaining similar salts, experiments have been conducted with *pp'*-dimethyldiethyldiaminodiphenylmethane. When this is treated with one molecular proportion of benzyl bromide or allyl iodide, normal addition takes place (Fröhlich, A., 1911, i, 493), but *sec*-butyl iodide does not react, and propyl bromide or iodide, and *isobutyl* and ethyl iodides give abnormal products of the type $2[\text{CH}_2(\text{C}_6\text{H}_4\cdot\text{NMeEt})_2]\cdot\text{RX}$.

The abnormal propiodide has been studied most completely. Attempts to convert it into the corresponding chloride, bromide, nitrate, or camphorsulphonate give rise to the free ditertiary base and the normal amino-ammonium salt, which can be precipitated as the normal iodide on the addition of potassium iodide. Silver oxide gives the same result. By treatment with silver perchlorate, however, an abnormal perchlorate may be obtained. The salt is also decomposed into the base and normal iodide by the action of aqueous-alcoholic ammonia, and benzyl bromide reacts in a manner which is to be interpreted in the same way.

The normal iodide combines with the base to form the abnormal salt, and reacts with benzyl bromide to form a salt with two unlike asymmetric nitrogen atoms of the desired type. Attempts to resolve this into the expected four optical isomerides gave no definite results.

The "*abnormal propiodide*," $(\text{C}_{19}\text{H}_{26}\text{N}_2)_2\cdot\text{C}_3\text{H}_7\text{I}$, is best obtained by heating equimolecular proportions of the base (Fröhlich, *ibid.*) and propyl iodide at 100° in a sealed tube. It crystallises from methyl alcohol with m. p. 153° , and its solutions become deep blue on exposure to the air. The abnormal perchlorate has m. p. $133\cdot5^\circ$. The normal iodide, *methylethylpropyl-methylethylamino-diphenylmethane-ammonium iodide*,

$\text{NMeEt}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMeEtPrI}$, has m. p. $158\cdot5^\circ$, the corresponding *nitrate* has m. p. $155\cdot5^\circ$, and the first crystals of the *d-camphorsulphonate* have $[\text{M}]_D + 59\cdot72^\circ$, which is about the same as that of the anion itself.

Diphenylmethanediammonium-(methylethylpropyl iodide)-(methyl-ethylbenzyl bromide),

$\text{NMeEt}(\text{C}_7\text{H}_7)\text{Br}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMeEtPrI}$, obtained by the action of benzyl bromide on the normal iodide, is separated by alcohol into a sparingly soluble fraction, decomp. about 175° , and a semi-solid portion. The *di-iodide* corresponding with the first fraction has m. p. 187° , and the *diperchlorate*, m. p. 225° , whilst the salts of the second portion have m. p.'s 182° and 222° respectively. The mixture of diperchlorates has m. p. 221° , and can be isolated from the product of the action of benzyl bromide on the abnormal iodide.

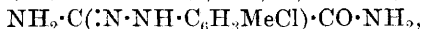
The base also forms an "*abnormal ethiodide*," m. p. $144\text{--}145^\circ$, and "*abnormal isobutiodide*," m. p. $140\text{--}141^\circ$, but methyl iodide converts it into *diphenylmethane-pp'-bisdimethylethylammonium di-iodide*, $\text{CH}_2(\text{C}_6\text{H}_4\cdot\text{NMe}_2\text{EtI})_2$, colourless needles, m. p. 203° .

J. C. W.

I. Syntheses and Reactions of New Monoaryl-hydrazidine Carboxylic Esters. II. Oxidative Fission by means of Chlorine of Organic Substances containing the Hydrazone and Hydrazidrazone Groups. (I.) CARL BÜLOW and RICH. ENGLER. (II.) CARL BÜLOW (*Ber.*, 1919, **52**, [B], 632—651).—In continuation of the work of Bülow and Engler (this vol., i, 47), the authors have now prepared ethyl α -aminoglyoxylate 3-chloro-*p*-tolylhydrazone, the corresponding amide and hydrazide, and have made an extended study of their reactions. They are led to the following general conclusions: Benzaldehyde arylhydrazones and their derivatives are primarily converted into pure chlorinated products by treatment with chlorine in a suitable solvent; as secondary change, the hydrazone is converted into the corresponding diazonium or chloroaryldiazonium group. The arylhydrazone residue is eliminated from hydrazidines or amidrazones as diazonium salt by the agency of chlorine. Nitrogen is eliminated by chlorine from acid hydrazidrazones and azines, but the fate of the remainder of the molecule has not yet been elucidated.

*Ethyl α -aminoglyoxylate-3-chloro-*p*-tolylhydrazone* is obtained as colourless, shining leaflets, m. p. 86° , by the action of alcoholic ammonia at the ordinary temperature on ethyl α -chloroglyoxylate-3-chloro-*p*-tolylhydrazone. The *hydrochloride* has m. p. 173 — 174° . The ester is readily decomposed by chlorine in acetic acid solution, and the diazonium salt of 3-chloro-*p*-toluidine which is produced is readily identified by coupling it with β -naphthol, the *product* forming long, red needles, m. p. 179 — 179.5° . Boiling concentrated aqueous hydrochloric acid decomposes the ester, yielding ammonium chloride, oxalic acid, and 3-chloro-*p*-tolylhydrazine hydrochloride; on account of its instability, the free base was not investigated. It reacts with *m*-nitrobenzaldehyde to yield *m*-nitrobenzaldehyde-3-chloro-*p*-tolylhydrazone, m. p. 175° , which is decomposed by nitric acid with production of a diazonium salt; this, with chlorine in acetic acid solution, gives the *substance*, $C_{14}H_{12}O_2N_3Cl$, long, yellow needles, m. p. 139° . 2:5-Dichlorobenzaldehyde-3-chloro-*p*-tolylhydrazone, slender needles, has m. p. 108° , and also yields a diazonium salt when treated with concentrated nitric acid, and a *substance*, m. p. 114 — 115° , when acted on by chlorine. The constitution of the hydrazine is definitely decided by preparation of the condensation products with *m*-nitrobenzaldehyde and 2:5-dichlorobenzaldehyde from synthetic 3-chloro-*p*-tolylhydrazine, and the identity of the products thus obtained with those previously prepared.

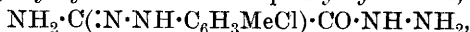
*α -Aminoglyoxylamide-3-chloro-*p*-tolylhydrazone.*



thick, greyish-white needles, m. p. 170 — 171° , is prepared by the more protracted action of alcoholic ammonia on ethyl α -chloroglyoxylate 3-chloro-*p*-tolylhydrazone; it is completely decomposed by nitric acid, and is quantitatively decomposed by chlorine, yielding a diazonium salt and a *substance*, $C_9H_{11}ON_4Cl$. The hydrazone

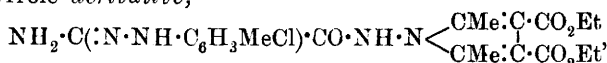
may also be prepared from α -chloroglyoxylamide-3-chloro-*p*-tolylhydrazone.

*α -Aminoglyoxylhydrazide-3-chloro-*p*-tolylhydrazone,*



colourless prisms, m. p. 199°, prepared by the action of hydrazine hydrate on the corresponding ester, is immediately decomposed by nitric acid, and undergoes oxidative fission by chlorine in a complicated manner, yielding large amounts of diazo-compound. The hydrazide readily yields *compounds* with benzaldehyde (yellow, rhombic leaflets, m. p. 203°), *p*-hydroxybenzaldehyde (pale yellow needles, m. p. 245°), *m*-hydroxybenzaldehyde (crystalline powder, m. p. 234°), 2:5-dichlorobenzaldehyde (yellow prisms, m. p. 262°), vanillin (small, colourless needles, m. p. 215°), and, less readily, with acetophenone (long needles, m. p. 229°). In each case, fission by chlorine occurs in two stages: (1) evolution of nitrogen, and (2) formation of diazonium salt. The compound with acetophenone is further remarkable for the ease with which it is decomposed into its constituents by concentrated hydrochloric acid.

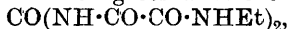
The hydrazide reacts also with ethyl diacetylsuccinate to yield the pyrrole *derivative*,



almost colourless rhombohedra, m. p. 228°. The compound is decomposed by nitric acid, yielding a diazonium salt, and also by chlorine; in the latter case, nitrogen is not evolved, the products being a diazonium salt and a residue containing the pyrrole nucleus.

H. W.

Diketopiperazines. VII. Action of Oxalyl Chloride on Alkylloxamides. J. V. DUBSKY and F. BLUMER (*Ber.*, 1919, **52**, [B], 215—217. Compare A., 1916, i, 635, 636, 672; 1918, i, 188, 189).—When alkylloxamides are heated with oxalyl chloride under reflux, they yield tetraketo-1-alkylpiperazines. Thus, methyl-oxamide forms the known methyl derivative, $\text{NMe} \begin{matrix} \text{CO} \cdot \text{CO} \\ \text{CO} \cdot \text{CO} \end{matrix} \text{NH}$, which confirms the constitution of this compound (*ibid.*, 636), whilst *tetraketo-1-ethylpiperazine* crystallises in small leaflets, m. p. 235°. Using benzene as a diluent, however, the compound obtained from ethylloxamide agrees with the formula

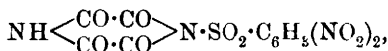


and has m. p. 175° (clear at 187°). Oxamide itself does not undergo such reactions.

J. C. W.

Diketopiperazines. VIII. Action of Absolute Nitric Acid on 3:5-Diketo-1-benzenesulphonylpiperazine. J. V. DUBSKY and F. BLUMER (*Ber.*, 1919, **52**, [B], 218—220).—3:5-Diketo-1-benzenesulphonylpiperazine is very stable towards

pure nitric acid, with which it only reacts on boiling, the product being a *compound*, probably of the formula

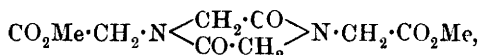


which forms a frothy mass at 124°, becoming clear at 130°.

The piperazine derivative was obtained by Johnson's method (A., 1906, i, 157) after the following alternative process was found to be fruitless. Methyl iminodiacetate is converted into its *benzenesulphonyl* derivative, needles, m. p. 55—57°, and then into *benzenesulphoniminodiacetamide*, $\text{SO}_2\text{Ph} \cdot \text{N}(\text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2)_2$, needles, m. p. 164°, which only loses a little ammonia when kept molten for an hour, and yields scarcely any sublimate when heated at 350°/10 mm.

J. C. W.

Diketopiperazines. IX. Action of Absolute Nitric Acid on 3:5-Diketo-1-ethylpiperazine. J. V. DUBSKY and F. BLUMER (*Ber.*, 1919, 52, [B], 221—225).—When methyl iminodiacetate is distilled, the residue apparently contains a condensation product, namely, *methyl 2:5-diketopiperazine-1:4-diacetate*,



m. p. 96—97°. The purified distillate (A., 1918, i, 188) is ethylated by means of ethyl sulphate, and the *methyl ethyliminodiacetate*, b. p. 111—113°/8 mm., is converted into *ethyliminodiacetamide*, $\text{NEt}(\text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2)_2$, by means of alcoholic ammonia. This has m. p. 137—140°, forms a *hydrochloride*, m. p. 206—208°, and a *nitrate*, m. p. 172°, and when heated at 250°/10 mm. gives a sublimate of 3:5-diketo-1-ethylpiperazine, $\text{NEt} \begin{array}{c} \text{CH}_2 \cdot \text{CO} \\ \text{CH}_2 \cdot \text{CO} \end{array} \text{NH}$, m. p. 74°. This yields a *hydrochloride*, small leaflets, and a *nitrate*, m. p. 145—148°, which dissolves in pure nitric acid to form a *compound*, $\text{C}_4\text{H}_5\text{O}_5\text{N}$, decomp. about 98°. J. C. W.

Diketopiperazines. X. J. V. DUBSKY [with ST. IZDEBSKA-DOMANSKA, M. SPRITZMANN, W. D. VAN LIER-WENSINK, and CH. GRÄNACHER] (*Ber.*, 1919, 52, [B], 225—234).—An account of the preparation of some diketopiperazines and their behaviour towards nitric acid.

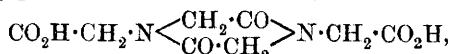
3:5-Diketo-1-phenylpiperazine.—This compound has been made in three ways: (a) by heating equal quantities of aniline and chloroacetamide at 120°, whereby the temperature suddenly rises to 210°, and then sinks again (Bischoff, A., 1889, i, 1015); (b) by heating phenyliminodiacetamide in a vacuum-sublimation apparatus (Bischoff, A., 1898, i, 10); (c) the best way, by heating together chloroacetamide and anilinoacetamide at 100—170°, the latter compound being prepared by heating aniline, chloroacetamide, and fused sodium acetate at 120—140°. When dissolved in ice-cold, absolute nitric acid, the piperazine forms a

yellow *dinitro*-derivative, $C_6H_5(NO_2)_2 \cdot N \begin{smallmatrix} CH_2 \cdot CO \\ CO \cdot CH_2 \end{smallmatrix} NH$, decomp. 105° .

3:5-Diketo-1:4-diphenylpiperazine.—Aniline and α -phenyliminodiacetic acid are condensed to the mono-anilide (Hausdörfer, A., 1889, 1013), and this is heated with benzene and acetic anhydride at 150 – 160° . The 3:5-diketo-1:4-diphenylpiperazine (*ibid.*) yields a mixture of di- and tri-nitro-derivatives with pure nitric acid.

3:5-Diketo-1-p-tolylpiperazine, glistening scales, m. p. 190 – 192° , from *p*-toluidine and chloroacetamide, forms a yellow *dinitro*-compound, m. p. about 110° (decomp.).

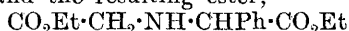
2:5-Diketopiperazine-1:4-diacetic acid,



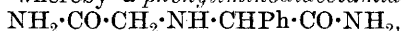
decomp. 280 – 290° , is not affected by solution in pure nitric acid.

2:5-Diketo-1-phenylpiperazine, pearly leaflets, m. p. 245° , obtained by the action of ammonia on chloroacetylphenylglycine (Leuchs and Manasse, A., 1907, i, 770), yields a sulphur-yellow *nitro*-compound, $NO_2 \cdot C_6H_4 \cdot N \begin{smallmatrix} CO \cdot CH_2 \\ CH_2 \cdot CO \end{smallmatrix} NH$, m. p. 247 – 252° .

Some attempts to prepare 3:5-diketo-2-phenylpiperazine are described. In the most successful scheme, glycine ester hydrochloride, benzaldehyde, potassium cyanide, ether, and water were shaken together, and the resulting ester,



(Stadnikoff, A., 1909, i, 106), was left with methyl-alcoholic ammonia at 0° , whereby α -phenyliminodiacetamide.

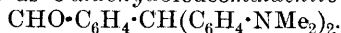


m. p. 152 – 153° , was formed. This did not, however, yield the expected piperazine on sublimation. J. C. W.

Mercury Mercaptide Nitrites and their Reaction with the Alkyl Iodides. V. Chain Compounds of Sulphur (*continued*).
SIR PRAFULLA CHANDRA RÂY and PRAFULLA CHANDRA GUHA (T., 1919, 115, 541–548).

Condensation Products of *o*-Phthalaldehyde. IV. Condensation of *o*-Phthalaldehyde with Dimethylaniline. ERNST WEITZ (*Annalen*, 1919, 418, 1–28. Compare Thiele and Weitz, A., 1910, i, 854).—This condensation follows very different courses according to the experimental conditions. When *o*-phthalaldehyde, dimethylaniline (more than 6 mols.), and anhydrous zinc chloride are heated together at 120 – 130° for two hours, the chief product is a *substance*, $C_{40}H_{46}N_4$, almost colourless, crystalline powder, m. p. 245° , which can only be the *leuco-base* of *o*-phthalaldehyde-green, $C_6H_4[CH(C_6H_4 \cdot NMe_2)]_2$. When *o*-phthalaldehyde, dimethylaniline (2 mols.), and anhydrous zinc chloride are heated together at 100 – 110° for one hour, the chief product is a *substance*, $C_{24}H_{26}ON_2$, crystals, brownish-red when massive, almost

colourless when powdered or in solution, m. p. 143—144°, which is converted into the preceding leuco-base by further heating with dimethylaniline and zinc chloride, reacts additively with acetic anhydride (1 mol.) in the presence of a few drops of sulphuric acid to form the *diacetate*, $C_{28}H_{32}O_4N_2$, m. p. 117—118°, and is therefore regarded as *o*-aldehydoleucomalachite-green,



By oxidation, both *leuco*-bases yield dyes which are almost olive-green.

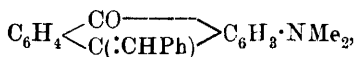
When *o*-phthalaldehyde and dimethylaniline are condensed by heating with concentrated hydrochloric acid on the water-bath, the product is a *substance*, $C_{24}H_{19}O_2N$, garnet-red leaflets, m. p. 163°, which behaves as a weak base (*picrate*, brown crystals, m. p. 170°, decomp. from about 150°). The substance reacts additively with 1 mol. of acetic anhydride (and sulphuric acid), forming a *diacetate*, $C_{28}H_{32}O_5N$, red prisms, m. p. 172°, yields a *nitro*-derivative, $C_{24}H_{18}O_4N_2$, red crystals, m. p. 183°, by treatment with aqueous sodium nitrite in 25% sulphuric acid solution, absorbs 1 mol. of hydrogen in acetone or 70% alcoholic solution by treatment by the Paal-Skita method, and 1 mol. of bromine in glacial acetic acid solution (in neither case could a well-defined additive product be isolated), and yields benzil-2:2'-dicarboxylic acid by oxidation with boiling alkaline permanganate solution. By oxidation in alcoholic solution at the ordinary temperature with 6% hydrogen peroxide solution and 2*N*-sodium hydroxide, the base yields 2-*p*-dimethylaminobenzoylbenzoic acid, *p*-dimethylamino-phenylphthalide, and a *lactone*, $C_{24}H_{19}O_3N$, yellow crystals, m. p. 163°.

On the evidence of the preceding reactions, the red base, $C_{24}H_{19}O_2N$, might be dimethylamino-*o*-aldehydobenzylidene-anthrone, $CHO \cdot C_6H_4 \cdot CH : C \begin{smallmatrix} \swarrow C_6H_4 \\ \searrow C_6H_3(NMe_2) \end{smallmatrix} > CO$, or 2-*o*-aldehydo-

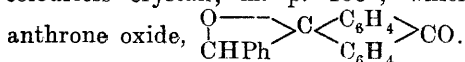
phenyl-3-*p*-dimethylaminophenylindone, $CHO \cdot C_6H_4 - C \begin{smallmatrix} \diagup CO \\ \diagdown C_6H_4 \cdot NMe_2 \end{smallmatrix} \cdot C \begin{smallmatrix} \diagup C_6H_4 \\ \diagdown C_6H_4 \end{smallmatrix}$. Since, however, 10-benzylideneanthrone and 2-dimethylamino-10-benzylideneanthrone (following abstract) respectively yield anthraquinone and 2-dimethylaminoanthraquinone by oxidation, whilst 2:3-diphenylindone yields phenylphthalide and *o*-benzoylbenzoic acid, there can be little doubt that the red base, $C_{24}H_{19}O_2N$, is 2-*o*-aldehydophenyl-3-*p*-dimethylaminophenylindone. C. S.

Some Anthrone Derivatives. E. WEITZ (*Annalen*, 1919, **418**, 29—35).—2-Dimethylaminoanthrone is best obtained by heating 2-*p*-dimethylaminobenzoylbenzoic acid with 96% sulphuric acid for one hour at 65—70° (the higher limit must not be exceeded), pouring the cooled solution into water, and neutralising with sodium carbonate. When heated with benzaldehyde (1 mol.) in pyridine containing a few drops of piperidine in a sealed tube at 100°, or, less satisfactorily, with concentrated hydrochloric acid on the water-

bath, it yields 2-dimethylamino-10-benzylideneanthrone,



red needles, m. p. 173°. The latter in alcoholic solution is oxidised to 2-dimethylaminoanthraquinone by 5% hydrogen peroxide and 2*N*-sodium hydroxide. Benzylideneanthrone under similar conditions of oxidation yields anthraquinone and a substance, $\text{C}_{21}\text{H}_{14}\text{O}_2$, colourless crystals, m. p. 133°, which is possibly benzylidene-



C. S.

3-Methyluric Acid. HEINRICH BILTZ and MYRON HEYN (*Ber.*, 1919, 52, [B], 768—784).—It has been recently shown (Biltz and Heyn, A., 1917, i, 291) that δ -, α -, and ζ -methyluric acids are in reality 3-methyluric acid, a mixture of 3-methyluric acid with about 25% 9-methyluric acid and a mixture of 90% of the 3- with 10% of the 9-isomeride respectively. The present communication contains further data in this connexion.

Traube's acid is shown to be 3-methyluric acid, and his process affords the best means of preparing this substance.

The action of chlorine on 3-methyluric acid has been further studied with larger quantities of material; when moisture is carefully excluded, a crystalline 5(4)-chloro-3-methylisouric acid is obtained, which slowly decomposes above 150° and which is reduced by potassium iodide to 3-methyluric acid. Like the amorphous preparation previously described, it is converted by methyl and ethyl alcohols into the corresponding glycol ethers, m. p.'s 207° (decomp.) and 203° (decomp.) respectively. Attempts to convert it into 5(4)-alkyloxy-3-methylisouric acids or 3-methyluric glycol diethers were unsuccessful. It is converted by water into methylalloxan and carbamide, a reaction which is of interest, since it affords an explanation of the ready isolation of 5-chloro-9-methyl- ψ -uric acid from crude α -methyluric acid, the 3-methyluric acid in these circumstances being transformed into products which are readily soluble. In complete absence of moisture, chlorination of the " α "-acid proceeds differently, the 3-methyluric acid being converted into chloro-3-methylisouric acid, whilst 9-methyluric acid yields a product closely allied to the parent substance, probably either 4-chloro-9-methyl- $\Delta^{5:7}$ -isouric acid or 9-methyluric acid 4:5-dichloride.

Attempts are described to isolate 3-methyl- and 9-methyluric acids from " α -methyluric acid" by means of the chloropurines. The action of phosphoryl chloride appears to follow a similar course with each isomeride, and separation was not found possible by conversion into chloropurines and regeneration of the acids from these by means of hydrochloric acid. The chloropurines, however, could be separated by means of their barium salts. From the more sparingly soluble, 8-chloro-3-methylxanthine, decomposing at 344°, was obtained, whilst the more soluble salt yielded 2:6-dichloro-8-

hydroxy-9-methylpurine, decomposing at 275—276°. The latter is quantitatively converted by hydrochloric acid into 9-methyluric acid, but the corresponding yield of 3-methyluric acid is poor. The process affords further evidence of the nature of " α -methyluric" acid, but is without quantitative or preparative significance.

The solubility of derivatives of uric acid in boiling water is frequently described as a means of identification or differentiation. For this purpose, highly accurate values are not required provided that all determinations are performed in a uniform manner. The authors recommend the gradual addition of weighed amounts of finely powdered material to a known volume of water, which is kept gently boiling; the saturation point is regarded as attained when a permanent uniform turbidity appears through the whole solution.

H. W.

α -, ζ -, and δ -Methyluric Acids. HEINRICH BILTZ and MYRON HEYN (*Ber.*, 1919, **52**, [B], 784—804).—The three "isomeric" 3-methyluric acids have been recently examined by Biilmann and Bjerrum (*A.*, 1917, i, 177), who have been led to conclusions differing somewhat considerably from those of Biltz and Heyn (*A.*, 1917, i, 291); the authors have therefore re-examined these acids and repeated much of the work of the Danish chemists. The chief results may be summarised as follows.

ζ -Methyluric acid differs from 3-methyluric acid. It is not a definite chemical compound, but consists rather of mixed crystals of 3-methyluric acid monohydrate and (about 5%) 9-methyluric acid monohydrate. In its properties it closely resembles 3-methyluric acid, but is slightly more soluble in water and rather more easily attacked by phosphoryl chloride.

α -Methyluric acid is also a mixture of 3- and 9-methyluric acids containing about 30—35% of the latter (that is, rather more than had been previously found). In no case is an equimolar compound formed. A crystallisation compound, possibly formed from two molecules of the 3-methyl acid and one molecule of the 9-methyl acid, together with two molecules of water of crystallisation, appears to be formed in small amount. This view is supported by the observation that α -methyluric acid, when crystallised by the method of Biilmann and Bjerrum or by the authors' process, separates in large, shining platelets, which, when further crystallised, appear to be perfectly uniform. On the other hand, however, the relative proportion of the two isomerides seems to vary somewhat, and the water content is scarcely sufficiently constant for a definite chemical compound; in addition, the results of thermo-analytical investigation, which must be received with caution, are opposed to the idea of a compound. It is not at present possible to decide definitely between the two possibilities, mixed crystals or compound, but the authors incline to the former.

The increase in solubility due to admixture, and observed in some instances with α -methyluric acid, as compared with 3- and 9-methyluric acids, is interesting. Similar cases appear to have

been seldom investigated. The increased solubility of salicylic acid in the presence of dextrose, ethyl alcohol, and *isobutyl* alcohol has, however, been examined by Hoffmann and Langbeck (A., 1905, ii, 374), whilst Störmer, Grimm, and Laage (A., 1917, i, 647) have observed that stereoisomeric β -alkylcinnamic acids yield difficultly separable mixtures of lower solubility. H. W.

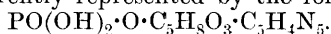
Substances which Inhibit the Coagulation of Proteins by Heat. G. MUNARETTO (*Arch. Pharm. experim.*, 1912, 460—468, 469—479; from *Bied. Zentr.*, 1919, 48, 128).—Formaldehyde and sulphurous acid are the most active inhibiting agents. Other reducing agents, arsenious acid, hydrogen sulphide, and sodium nitrite, are inactive. The addition of sulphurous acid or formaldehyde raises the viscosity of protein solutions. Ox serum becomes gelatinous on contact with sulphurous acid at the ordinary temperature. These effects suggest that a process of denaturation occurs. J. C. D.

Action of Acid and Alkali on Gluten. L. J. HENDERSON, EDWIN J. COHN, P. H. CATHCART, J. D. WACHMAN, and W. O. FENN (*J. Gen. Physiol.*, 1919, 1, 459—472).—Measurements of the hydrogen-ion concentration of solutions which had been in contact with powdered gluten show that the hydrogen-ion concentration in such systems is determined by the ratio of gluten to acid or base. The conclusion is reached that in systems containing gluten and acids or bases, the formation of salts, in accordance with the requirements of the mass law, is the fundamental phenomenon. Measurements were also made of the swelling and viscosity of the gluten component of such systems. The results indicate that simple chemical phenomena are most important in these systems, and that modifications of these, resulting from colloidal and heterogeneous characteristics, are of secondary importance in determining the condition of equilibrium, although somewhat more significant in the progress of the system toward the condition of equilibrium. J. C. D.

Steric Hindrance of Methyl Groups in the Nucleus. WOLFGANG HEUBNER (*Biochem. Zeitsch.*, 1919, 93, 395—396).—Certain aniline derivatives induce blood changes, with the formation of methæmoglobin, when administered to animals. This toxic action may be greatly reduced by the introduction of two methyl groups in the ortho-ortho- or the ortho-para-positions to the nitrogen group (compare A., 1913, i, 786). It is considered that the steric hindrance of the methyl groups prevents oxidation of the nitrogen group, which the author holds is necessary before methæmoglobin can be formed. J. C. D.

Adenine Mononucleotide. WALTER JONES and R. P. KENNEDY (*J. Pharmacol. Exp. Ther.*, 1918, 12, 253).—A crystalline

product, $C_{10}H_{14}O_7N_5P \cdot H_2O$, has been prepared from yeast-nucleic acid. It is soluble in hot water, but very slightly so in cold. It gives the colour reactions for pentose and forms a brucine salt with two equivalents of brucine. Hydrolysis with dilute sulphuric acid yields adenine, but no guanine. Its entire phosphoric acid is readily split, so that it contains neither a cytosine nor a uracil group. It is apparently represented by the formula



J. C. D.

Amphoteric Colloids. II. Volumetric Analysis of Ion-Protein Compounds; the Significance of the Isoelectric Point for the Purification of Amphoteric Colloids.

JACQUES LOEB (*J. Gen. Physiol.*, 1918, 1, 237—254).—At the isoelectric point, $p_H=4.7$, gelatin is practically not dissociated at all. By volumetric analysis, it has been shown that on the alkaline side of the isoelectric point gelatin can combine with cations only, whilst on the acid side it can combine with anions only. At the isoelectric point, gelatin (and probably amphoteric colloids generally) must give off any ion with which they are combined. The simplest method for obtaining these colloids approximately free from inorganic impurities would therefore seem to consist in bringing their hydrogen-ion concentration to that characteristic of their isoelectric point. When gelatin is in combination with univalent ions (Ag, Br, CNS), the curve representing the amount of ion-gelatin present is approximately parallel to the curves for swelling, osmotic pressure, and viscosity. This proves that the influence of the ions on these properties is determined by the chemical or stoichiometrical, and not by the "colloidal," properties. The sharp drop of these curves at the isoelectric point finds its explanation in the equal drop of the water-solubility of pure gelatin. It is not yet possible to state whether this is merely due to a lack of ionisation of gelatin or to the formation of a tautomeric or polymeric compound. A slight change in the hydrogen-ion concentration increases the water-solubility of gelatin near the isoelectric point. This is not produced by treatment with any other kind of univalent or multivalent ion, and it is considered that this is in harmony with a chemical conception of proteins rather than with the adsorption theory of colloids.

J. C. D.

Amphoteric Colloids. III. Chemical Basis of the Influence of Acid on the Physical Properties of Gelatin.

JACQUES LOEB (*J. Gen. Physiol.*, 1919, 1, 363—385. Compare preceding abstract).—The influence of hydrobromic acid on the physical properties of gelatin has a purely chemical or stoichiometrical basis. Gelatin is an amphoteric colloid which is sparingly soluble in water at its isoelectric point, whilst transformation into a salt with a univalent ion makes it soluble. Hence the curves representing the changes in osmotic pressure, viscosity, and swell-

ing of gelatin are approximately parallel to those representing the amount of bromine bound by the gelatin.

Titration with sodium hydroxide of gelatin, previously treated with hydrobromic acid, and therefore being on the acid side of its isoelectric point, results in the neutralisation of the pure gelatin (NaOH isoelectric) with sodium hydroxide, and besides in the neutralisation of the hydrobromic acid in combination with the gelatin.

J. C. D.

Amphoteric Colloids. IV. The Influence of the Valency of Cations on the Physical Properties of Gelatin. JACQUES LOEB (*J. Gen. Physiol.*, 1919, 1, 483—504. Compare preceding abstracts).—The amount of equivalents of metal in combination with 1 gram of a 1% gelatin solution previously treated with an alkali can be ascertained when the excess of alkali is washed away and the hydrogen-ion concentration determined. The results of experiments with lithium, sodium, potassium, ammonium, calcium, and barium hydroxides show that twice as many univalent ions as bivalent cations combine with the same mass of gelatin.

The curves representing the influence of lithium, sodium, potassium, and ammonium on the osmotic pressure (and the other physical properties) of gelatin are identical, using p_H as abscissæ. This contradicts the statements current in colloid chemistry, according to which these four cations have a different effect. The curves for calcium and barium gelatinates are also identical, but differ from those for the univalent metals examined. The ratio of the maximal osmotic pressures of the two groups is 1:3. This means that in a 1% solution of a metal gelatinates there are approximately three times as many particles in solution or suspension when the metal is univalent as when it is bivalent.

The curves representing the conductivities of the same gelatin solutions are almost identical (for the same p_H).

The curves for the viscosity and swelling of barium or calcium and sodium gelatinates are approximately parallel to those for osmotic pressure. The practical identity of the conductivities of metal gelatinates with univalent and bivalent metals excludes the possibility that the differences observed in the osmotic pressure, viscosity, and swelling are determined by differences in degree of ionisation. If it is assumed that compounds of the type $\text{Ca}(\text{gelatin})_2$ exist, the two anions of which can form one aggregate of two gelatin anions, and that such aggregates can form larger aggregates of four, six, and eight gelatin anions, every one of which keeps its original charge, it would be possible to account for the phenomena observed.

J. C. D.

Physiological Chemistry.

Bioelements : The Chemical Elements of Living Matter.

INGO. W. D. HACKH (*J. Gen. Physiol.*, 1919, **1**, 429—433).—The distribution of the elements which enter into the composition of living matter is considered with reference to a new periodic classification (Hackh, A., 1918, ii, 306, 396). J. C. D.

An Indicator Method of Measuring the Consumption of Oxygen. W. J. V. OSTERHOUT (*J. Gen. Physiol.*, 1918, **1**, 167—169).—The blood of *Limulus* when shaken with air absorbs oxygen and turns blue. In the presence of certain organisms which consume oxygen, it is quickly decolorised. A method is described for measuring the time required for the colour change, from which the rate of consumption of oxygen may be determined. J. C. D.

Chemical Studies in Physiology and Pathology. VI. The Biochemistry of Oxidation (Cell Respiration; Oxidising Enzymes; The Theory of Narcosis). E. HERZFELD and R. KLINGER (*Biochem. Zeitsch.*, 1919, **93**, 324—352).—The atoms of the oxygen molecule can be activated by the formation of certain molecular compounds. In aqueous solution, oxygen may form a compound represented by the formula
$$\begin{array}{c} \text{H} \\ | \\ \text{H} > \text{O} \cdots \text{O} \cdots \text{O} \cdots \text{O} < \text{H} \\ | \\ \text{H} \end{array}$$

This linking expresses the activity of the complex H_4O_4 . In this manner, complexes can be formed with water or metals in the form of peroxides. Oxygen bound in this manner can oxidise to carbon dioxide and water many organic substances, such as the lower fatty acids or their salts, without assistance.

The oxidative processes of the body are concerned with the oxidation of simple degradation products derived from the complex proteins, fats, and polysaccharides, and for this purpose the presence of oxygen in the activated form is sufficient. The assumption of the existence of special oxidising enzymes is superfluous. The relationship of these processes to narcosis and respiration is discussed. J. C. D.

The Presence of Calcium in the Red Blood Corpuscles of Ox and Man.

DAVID MURRAY COWIE and HENRIETTA A. CALHOUN (*J. Biol. Chem.*, 1919, **37**, 505—509).—The red blood corpuscles contain calcium, but in a somewhat smaller concentration than the serum (compare Marriott and Howland, A., 1918, ii, 21). J. C. D.

Simultaneous Oxidation of Blood and of Dextrose.

R. FOSSE (*Compt. rend.*, 1919, **168**, 908—910. Compare A., 1912, i, 541).—If, under suitable conditions, the proteins of blood and

dextrose are oxidised simultaneously, there is marked formation of carbamide. The yield of carbamide, formed by the oxidation of blood to which dextrose has been added, increases, within certain limits, with the proportion of dextrose and oxygen consumed. Under suitable conditions, the amount of carbamide formed may reach to 40 grams per litre of blood. W. G.

The Nutritive Value of the Wheat Kernel and its Milling Products. THOMAS B. OSBORNE and LAFAYETTE B. MENDEL [with the co-operation of EDNA L. FERRY and ALFRED J. WAKEMAN] (*J. Biol. Chem.*, 1919, **37**, 557—601).—The proteins of the entire wheat kernel are not greatly inferior for maintenance to caseinogen, edestin, or even to the total proteins of milk, but they are somewhat superior to gliadin. The wheat proteins considered in their entirety are sufficient for the growth of rats if consumed in sufficient amount. The quantity required is, however, relatively large when comparisons with proteins such as caseinogen are made.

The "crude protein" of commercial wheat embryo meal is more efficient for maintenance than that of the entire kernel or of the endosperm, and it is much more efficient for growth than endosperm protein. The protein of commercial wheat bran may be well utilised (70—75%) by the rat, and if eaten in sufficient amount may be considered somewhat superior to that of commercial embryo and decidedly superior to that of endosperm in promoting growth.

The proteins of the endosperm are adequate for maintenance, but inadequate for growth. Additions of meat, milk, and eggs to wheat flour greatly enhance the value of the proteins of the latter foodstuff for growth.

Commercial wheat embryo is rich in the water-soluble vitamine, but the pure isolated embryos do not appear to contain it. Evidence is given which indicates that the accessory factor is localised in the endosperm, although it is not uniformly distributed throughout it. No confirmation of the existence of a toxic substance in wheat has been obtained (compare Hart, Miller, and McCollum, A., 1916, i, 531).

The question of the degree to which wheat should be milled for general purposes is fully discussed, and the conclusion is reached that, except in special cases, little can be gained by including the bran and embryo in the flour when this is used under the dietary conditions prevailing in the United States. J. C. D.

The Origin of Formic Acid in the Organism. E. SALKOWSKI (*Zeitsch. physiol. Chem.*, 1919, **104**, 161—174).—Oxidation of glycerol with potassium permanganate in acid solution may yield as much as 24% of formaldehyde. An increased excretion of formic acid was observed to follow the administration of glycerol. It apparently arises by the intermediate formation of formaldehyde. Glycerophosphoric acid, choline, and lecithin all yield formaldehyde when oxidised by potassium permanganate in acid solution. There is no reason to suppose that the formic acid

excreted in the urine originates from one source. No doubt carbohydrates, glycerol, and lecithin all contribute a certain amount. 3% Hydrogen peroxide will oxidise lecithin, choline, and glycerophosphoric acid, with the formation of formaldehyde.

J. C. D.

Bioluminescence. VII. Reversibility of the Photogenic Reaction in Cypridina. E. NEWTON HARVEY (*J. Gen. Physiol.*, 1918, **1**, 133—145).—The author has previously described two photogenic substances from the ostracod crustacean *Cypridina hilgendorffii*, photogenin, which is destroyed by boiling and is non-dialysable, and photophelein, which is stable to boiling and may be dialysed (A., 1917, **i**, 365). It is now suggested that photophelein is a mixture of two substances, one of which is an oxidisable substance similar to luciferin from *Pholas dactylus* (Dubois, A., 1897, **ii**, 112). Photogenin is now termed *luciferase*. The term photophelein is retained for a substance present in the extracts which acts by setting free bound or adsorbed luciferin. The action of this substance may be imitated by sodium chloride crystals or saponin. Luciferin is oxidised to *oxyluciferin*, and it is not believed that the change involves a fundamental destruction of the molecule, as it is a reversible process. The change is not analogous to that of hæmoglobin, for it cannot be reversed by reducing the partial pressure of the oxygen. It resembles more closely the oxidation of methylene-blue. The conception of Dubois that luciferin is formed from a precursor proluciferin by the agency of an enzyme coluciferase is held to be incorrect, and the correct explanation is believed to be that oxyluciferin may be reduced to luciferin by a reducing enzyme. Oxyluciferin will pass through a porcelain filter and is dialysable. Luciferin does not exhibit reducing properties similar to those of dextrose. J. C. D.

Bioluminescence. IX. Chemical Nature of Cypridina Luciferin and Cypridina Luciferase. E. NEWTON HARVEY (*J. Gen. Physiol.*, 1919, **1**, 269—293).—Of a large number of enzymes investigated, only those possessing a proteolytic activity had any digestive effect on luciferase, whilst none had any action on luciferin. A study was made of the "salting out" of luciferin and luciferase, as well as of their solubilities in various solvents, and their behaviour when treated with certain precipitants. Both substances are somewhat readily adsorbed by bone-black, kaolin, and colloidal ferric hydroxide. Consideration of the results obtained in this investigation leads to the opinion that luciferin is a protein on the border-line between the proteoses and peptones, whilst luciferase is regarded as being a more complicated protein, but not a globulin. J. C. D.

Pharmacology of the Ureter. VI. Action of some Optical Isomerides. DAVID I. MACHT (*J. Pharmacol. and Exp. Ther.*, 1918, **12**, 255—263).—*l*-Hyoscamine and *l*-hyoscine stimulate

the contractions of the ureter, whereas *d*-hyoscamine and *d*-hyoscine have an inhibitory action. The action of atropine appears to be a summation of the action of the two optically active varieties. Inactive or racemic scopolamine shows an inhibitory action, which is ascribed to the preponderating effect of the *d*-component. *l*-Adrenaline is much more active in stimulating ureteral contractions and raising the tone of the ureters than the racemic variety. *d*-Adrenaline was not examined. *l*-Camphor produced a marked stimulation, but *d*-camphor was apparently inactive. The effect of the racemic form is represented by the arithmetical mean of the two components.

J. C. D.

Isomerism and Anæsthetic Action. J. MORGENROTH (*Ber. Deut. pharm. Ges.*, 1919, **29**, 233—250).—Comparison of the anæsthetic action of eucupine (*isoamylhydrocupreine*) dihydrochloride and *isoamylapohydroquinidine* dihydrochloride shows a quantitative difference between the activity of the stereoisomerides, the former being about twice as potent as the latter. Experiments with eucupine dihydrochloride and eucupinotoxin hydrochloride at different concentrations prove both structural isomerides to have anæsthetic action. The latter does not appear to depend on the intact quinuclidine nucleus, since a pronounced increase in anæsthetising action is coincident with rupture of the carbon-nitrogen bond. The corresponding toxin is far more potent than eucupine, and forms the most powerful anæsthetic known (forty to fifty times stronger than cocaine). It has the power of producing prolonged anæsthesia.

The author is led to the conclusion that the chemotherapeutic action towards trypanosomes, the disinfecting action towards different bacteria, and the anæsthetic action are common to the quinotoxins and to the original alkaloids, and that comparatively all three functions are exerted to a greater degree by the latter. The difference in activity of ethylhydrocupreine and ethylhydrocupreinotoxin towards pneumococci appears to be an exception. Anæsthetic action does not appear to depend actually on space arrangement, since, as shown by the above experiments, the differences are only quantitative. In one instance quoted in the literature, that of benzoyltropeine and benzoyl- ψ -tropeine, a marked difference in anæsthetising action has been attributed to difference in spatial configuration; re-examination of these substances has failed to disclose any difference in their activity.

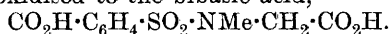
H. W.

Secondary Action of Arsenic and Salicylic Acid Preparations on the Normal Stomach. BRUNO LEICHTENTRITT (*Zeitsch. physiol. Chem.*, 1919, **104**, 154—160).—According to Klosman (*A.*, 1912, ii, 965), sodium salicylate causes a decreased secretion of gastric juice. This was not confirmed, for it was found that aspirin, sodium salicylate, and salol caused an increased flow. His results with Fowler's solution (liq. potass. arsenic) are, however, confirmed. This preparation, as well as certain organic arsenic

preparations, such as elarson and arsacetin, increased the flow of gastric juice. A similar result was obtained by the administration of preparations containing both iron and arsenic. J. C. D.

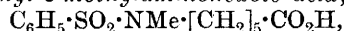
A New Instance of β -Oxidation in the Animal Body.

KARL THOMAS and HERBERT SCHOTTE (*Zeitsch. physiol. Chem.*, 1919, **104**, 140—153).—Oral administration of *p*-toluenesulphonylsarcosine to rabbits results in 80% being excreted in the urine unchanged; 4% is oxidised to the bibasic acid,



81% of benzenesulphonylsarcosine administered in the same manner was recovered from the urine.

ϵ -Benzenesulphonyl- ϵ -methylaminohexoic acid,



prepared from ϵ -methyl-leucine, crystallises from methyl formate and light petroleum in slender, white needles, m. p. 57° . When administered to rabbits, 44% was recovered from the urine as γ -benzenesulphonylmethylaminobutyric acid, oxidation having occurred at the β -carbon atom.

Benzenesulphonylaminobutyric acid, $\text{C}_6\text{H}_5\cdot\text{SO}_2\cdot\text{NH}\cdot[\text{CH}_2]_3\cdot\text{CO}_2\text{H}$, has m. p. 91 — 92° . When methylated with methyl sulphate, it yields *benzenesulphonylmethylaminobutyric acid*, m. p. 84 — 87° . This substance was recovered unchanged from the urine after administration to rabbits. J. C. D.

Detoxication of Inhaled Hydrogen Cyanide by Sodium Thiosulphate. E. TEICHMANN and W. NAGEL (*Biochem. Zeitsch.*, 1919, **93**, 312—323).—The observation of Lang (*Arch. exp. Path. Pharm.*, 1895, **36**, 75) that sodium thiosulphate can protect animals against the toxic effects of hydrogen cyanide is confirmed. The salt is efficient as an antidote when the poison is inhaled by animals. It will be necessary to establish that sodium thiosulphate is not toxic for man before the therapeutic application can be made. J. C. D.

Chemistry of Vegetable Physiology and Agriculture.

Influence of Different Agents on the Saccharifying and Fermenting Powers of *Mucor Boulard*. BETTINGER and DELAVALLE (*Bull. Assoc. Chim. Sucr.*, 1918, **35**, 114—129).—In experiments on the cultivation of *Mucor Boulard* on sugared extract of malt combs, the development of acid was found to be in direct proportion within limits to the access of air and the sugar content. Comparatively low temperatures gave the highest results. Succinic acid is the only non-volatile acid formed, whilst acetic acid mainly constitutes the volatile acidity. Nitrogenous matter

at first retards, but later accelerates, saccharification, peptone and asparagine giving the best results, whereas ammonium sulphate has a comparatively slight effect in this direction. Calcium and potassium phosphates, and to a less degree ammonium phosphate, accelerate saccharification, but sodium phosphate produces little or no result.

J. P. O.

The Sensitiveness of Living Yeast to H^+ and OH^- Concentration. H. VON EULER and F. EMBERG (*Zeitsch. Biol.*, 1919, **69**, 349—364).—Fermentation by the living cell is not effected solely by zymase, but is bound up to a large extent with the life of the cell itself. From the investigation of a bottom yeast, it is shown that the sensitiveness to acid and alkali of the process of inversion by the living yeast cell is not appreciably different from the sensitiveness of the isolated enzyme. It is therefore possible to conclude that the enzyme exists in the free state in the cell. The influence of growing the bottom yeast at different hydrogen-ion concentrations (p_H 3.5—3.8 and 6.6—7.2) on the characteristic cellular activities has been studied. The inverting action was little affected, but appreciable changes in the rate of growth and composition of the cells were noted.

J. C. D.

Changed Course of Alcoholic Fermentation in an Alkaline Medium. ALICE OELSNER and ALFRED KOCH (*Zeitsch. physiol. Chem.*, 1919, **104**, 175—181).—The authors have failed to confirm the statements of Wilenko (A., 1917, i, 680) that the course of the fermentation of sugar in an alkaline phosphate medium is changed and that no carbon dioxide is formed under those conditions. The alkalinity delays the fermentation, but alcohol and carbon dioxide are always obtained. The observation of Neuberg and Färber (A., 1917, i, 502) that more aldehyde is produced when the fermentation is conducted in an alkaline medium is confirmed.

J. C. D.

The Temperature-coefficient of Photosynthesis. W. J. V. OSTERHOUT and A. R. C. HAAS (*J. Gen. Physiol.*, 1919, **1**, 295—298).—The temperature-coefficient of photosynthesis in *Ulva rigida* between 17° and 27° is 1.81. It is suggested that photosynthesis involves catenary reactions of the type $S \rightarrow M \rightarrow P$, in which S represents a substance which, under the influence of light, breaks down to form M ; this in turn forms P , the amount of which is proportional to the amount of photosynthesis. If the reaction $S \rightarrow M$ is more rapid than $M \rightarrow P$, the speed of the reaction as a whole will depend chiefly on the speed of the change $M \rightarrow P$.

The effect on the whole reaction of a rise of temperature will therefore depend chiefly on its effect on the second reaction. It is therefore not surprising to find a high temperature-coefficient for photosynthesis. Analogous cases exist in photochemistry.

J. C. D.

Permeability in Plants. W. J. V. OSTERHOUT (*J. Gen. Physiol.*, 1919, **1**, 299—304).—Certain conclusions concerning the behaviour of protoplasm drawn from the results of experiments on *Laminaria Agardhii* (compare A., 1918, i, 470) have been confirmed by experiments with a red alga (*Rhodomenia palmata*), a green alga (*Ulva rigida*), and a flowering plant (*Zostera marina*).
J. C. D.

Decrease of Permeability and Antagonistic Effects caused by Bile Salts. W. J. V. OSTERHOUT (*J. Gen. Physiol.*, 1919, **1**, 405—408).—The results of experiments on the electrical conductivity of *Laminaria* indicate that sodium taurocholate is able to produce a decrease in permeability and to antagonise sodium chloride. This confirms the hypothesis that antagonistic relations can be predicted from studies on the permeability of pure substances.
J. C. D.

A Comparison of Permeability in Plant and Animal Cells. W. J. V. OSTERHOUT (*J. Gen. Physiol.*, 1919, **1**, 409—413).—The author has made quantitative studies of the permeability of plant cells as represented by *Laminaria*, and animal cells as represented by the skin of frogs (*Rana pipiens*). Both tissues showed a closely similar behaviour, and this agreement indicates that the conclusions drawn from a study of *Laminaria* are of general application. It would appear that the physiological characteristics brought to light by these studies belong to the fundamental properties of protoplasm.
J. C. D.

Effect of certain Compounds of Barium and Strontium on the Growth of Plants. J. S. MCHARGUE (*J. Agric. Res.*, 1919, **16**, 183—194).—Barium or strontium carbonate in the absence of calcium carbonate is toxic to plants, the former having a greater toxicity than the latter, but in the presence of calcium carbonate they appear to exert a distinct stimulating influence on the growth of the plants studied. Barium sulphate is much more toxic than barium carbonate. Neither barium nor strontium can replace calcium as a plant food. The root growth is accelerated in all cases where barium or strontium carbonate is added to the sand in which the plants are growing. W. G.

The Identification, Localisation, and Distribution of Oxalic Acid [Soluble Oxalates] in Plants. NORBERT PATSCHOVSKY (*Ber. Deut. bot. Ges.*, 1918, **36**, 542—548).—The usual method of detecting the presence of soluble oxalates in cell sap by means of potassium salts suffers under the disadvantages that the potassium oxalate crystals are not very characteristic, and that they are liable to be completely obscured by co-precipitated tannins. The author finds ferrous sulphate or ferrous ammonium sulphate to be a more suitable reagent; the not too thin section is immersed on an object-glass in an acetic acid solution of the ferrous salt (10%), covered

with a slip, and gently warmed to expel air; in the presence of oxalates, ferrous oxalate separates after a time in crystals, the size of which is about $15 \times 9 \mu$. Larger crystals may be obtained by delaying the separation by addition of sodium acetate, sucrose, or gelatin.

The localisation of oxalates is best effected by injecting a highly concentrated ferrous solution into the plant by means of an air pump; under these conditions, precipitation of ferrous oxalate occurs within the cell, whilst with less concentrated solutions the oxalates diffuse through the cell wall, and precipitation takes place in the intercellular region.

The ferrous reagent has the further advantage of allowing a simultaneous detection of tannins.

The author has applied the method to a large number of plants; for details, the original paper must be consulted. H. W.

Action of Coal Gas on Plants. V. Action on Trees. Hydrocyanic Acid as the most Detrimental Constituent of Gas. C. WEHMER (*Ber. deut. Bot. Ges.*, 1918, **36**, 460—464. Compare A., 1917, i, 618; this vol., i, 114).—Continuing his previous experiments on the action of coal gas on the root systems of trees, the author now finds that in many instances in which the detrimental action is not immediately apparent, the effects are observed at the end of the period of winter rest, when in almost every instance the tree is killed. The most detrimental constituent of coal gas is now proved to be hydrogen cyanide; the toxicity of gas-water is shown to be exactly similar to that of a hydrocyanic acid solution of equivalent concentration, and, further, the violent toxic action of coal gas is not observed if the gas is passed through a solution of alkali hydroxide and ferrous sulphate. Cress is extraordinarily sensitive to minute traces of hydrocyanic acid. H. W.

A Purely Mineral Solution Capable of Assuring the complete Evolution of Maize Cultivated and Sheltered from Bacteria. P. MAZÉ (*Ann. Inst. Pasteur*, 1919, **33**, 139—173).—From a series of water-culture experiments, the author finds that, in addition to nitrogen, phosphorus, potassium, calcium, magnesium, sulphur, iron, chlorine, silicon, manganese, and zinc, boron, aluminium, fluorine, and iodine are equally essential to the development of maize. Organic substances, excluding the organic reserves of the seed, although not indispensable, exert a beneficial influence on the growth of the plant when added to the mineral nutrient solution. It is advisable that the iron should be present in the ferric state in the culture solution, or that some oxidising agent should be present. Insufficient aeration of the culture solution exerts an unfavourable influence on the vegetation. W. G.

Organic Chemistry.

Electrolytic Preparation of Chloroform. JOSEF FEYER (*Zeitsch. Elektrochem.*, 1919, **25**, 115—145).—The electrolytic preparation of chloroform from alcohol and from acetone has been investigated under various conditions, particularly in solutions of alkali chlorides and chlorides of the alkaline earth metals. It is shown that the methods put forward in the literature for the electrolytic preparation of chloroform from acetone are inaccurate in their details on account of imperfect methods of analysis. It is also shown that the present methods of isolating the chloroform are imperfect; this applies both to the method of absorption of the chloroform in alcohol and to the distillation method. Both methods involve considerable loss of material. Pure chloroform can only be directly obtained by freezing it out of its mixture with hydrogen by means of solid carbon dioxide and ether. The present methods of electrolysis are inefficient, because the alkali produced in the process decomposes considerable quantities of chloroform. By using a neutralisation cathode, it is possible to prepare chloroform from acetone in yields amounting to 65% of the current. When platinum electrodes are used, a material yield of 75—80% is obtained with a current density of 1.1 amp./sq. cm. at the anode and 0.5 amp./sq. cm. at the cathode. The primary reaction in the electrolysis is the formation of hypochlorite, which is followed by the reaction $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_3 + 3\text{HOCl} = \text{CHCl}_3 + \text{CH}_3\cdot\text{CO}_2\text{H} + 2\text{H}_2\text{O}$. Methyl ethyl ketone and higher ketones react in the same way with electrolytic hypochlorite. The method for the preparation of chloroform from alcohol put forward by Trechzinsky (A., 1907, i, 270) is criticised and shown to be inaccurate. In the case of alcohol, it is also possible by the introduction of a neutralisation cathode to obtain considerable yields of chloroform at temperatures between 25° and 35° when a current density of 1 amp./sq. cm. is used on the anode and 1.5 amp./sq. cm. on the cathode. A current yield of 77% and a material yield of 82% were obtained under these conditions. The maximum yield is obtained at temperatures between 25° and 30°. The preparation of chloroform from acetone or alcohol in calcium chloride solution only proceeds well when specially prepared nickel or copper cathodes are used. These electrodes are prepared by immersing ordinary nickel or copper electrodes in concentrated nitric acid for a few moments and then washing with water. Using these electrodes, a current yield of 71% and a material yield of 80% were obtained from acetone in calcium chloride, whilst with alcohol in calcium chloride the material yield was 99% and the current yield 90%. The formation of chloroform from alcohol occurs in three stages: first, an oxidation of the alcohol to aldehyde; secondly, a formation of hypochlorite; and thirdly, an interaction between the

aldehyde and the hypochlorite: (i) $\text{CH}_3\cdot\text{CH}_2\cdot\text{OH} + \text{HOCl} = \text{CH}_3\cdot\text{CHO} + \text{H}_2\text{O} + \text{HCl}$; (ii) $\text{OH}' + \text{Cl}_2 = \text{H}' + \text{Cl}' + \text{ClO}'$; (iii) $\text{CH}_3\cdot\text{CHO} + 3\text{HOCl} = \text{CHCl}_3 + \text{HCO}_2\text{H} + 2\text{H}_2\text{O}$; (iv) $\text{H}\cdot\text{CO}_2\text{H} + \text{HOCl} = \text{CO}_2 + \text{H}_2\text{O} + \text{HCl}$. It is shown that equation (i) is partly replaced by the reaction $\text{CH}_3\cdot\text{CH}_2\cdot\text{OH} + \text{O} = \text{CH}_3\cdot\text{CHO} + \text{H}_2\text{O}$.

J. F. S.

Substitution by Halogens in the Aliphatic Series. OSSIAN ASCHAN (*Finska Kem. Medd.*, 1918, 10 pp.; from *Chem. Zentr.*, 1919, i, 221).—The catalytic influence of light on the process of chlorination probably depends on the formation of the complex, Cl_3 , in illuminated chlorine. The catalysing action of water is attributed to the production of a hydrate, $\text{H}_2\text{OCl}_2 + n\text{H}_2\text{O}$, which only actually separates below 0° , but is assumed to be capable of transitory existence at a higher temperature. The presence of water during chlorination is particularly advantageous in the treatment of readily volatile hydrocarbons. The method of moist chlorination has been applied in particular to substituted hydrocarbons, such as ethyl chloride, *iso*amyl chloride, ethylene chloride, chloroform, propyl bromide, ethylene bromide, ethyl iodide, toluene, and xylene.

H. W.

Organic Chemical Reagents. IV. The Preparation of Alkyl Iodides. ROGER ADAMS and V. VOORHEES (*J. Amer. Chem. Soc.*, 1919, **41**, 789—798).—The usual laboratory methods for the preparation of the alkyl iodides are unsuitable when dealing with large quantities of material. The rapid preparation of methyl, ethyl, *n*-butyl and *iso*amyl iodides (in quantities of 3—4 kilos.) according to a modification of Walker's method (*T.*, 1892, **61**, 717) is fully described, along with a detailed account of the apparatus employed. *n*-Propyl iodide was prepared in smaller amount.

The suitable alcohol is heated in a large, round-bottomed flask of about 12 litres capacity with a mixture of approximately equal amounts of red and yellow phosphorus. The vapours evolved are condensed in contact with iodine, and are then returned to the flask. The use of a certain amount of yellow phosphorus is particularly advantageous, the reaction then being instantaneous and the colour of the iodine disappearing immediately on reaching the reaction flask. During the subsequent distillation of the alkyl iodides, the troublesome frothing which occurs when only red phosphorus is employed is absent. Further quantities of iodine can be introduced without dismantling the apparatus, and it is possible to prepare more than 6 kilos. of crude iodide in a day, using enough phosphorus and alcohol for four portions of iodine of $1\frac{1}{2}$ kilos. each. Five such apparatus can easily be run simultaneously, producing 30 kilos. of crude product in a day.

In the case of butyl and amyl alcohols, the reaction proceeds extremely readily, owing to the great solvent action of these compounds on iodine at their boiling point. A small amount of yellow

phosphorus is always left behind, but phosphonium compounds do not appear to be formed. The yields are in every case 90—100% of the theoretical.

In the preparation of the lower alkyl haloids, a large excess of alcohol may be used, but in the case of the higher alcohols this must be avoided, as otherwise difficulties arise in the purification of the product.

F. C.

Nitroethylene. HEINRICH WIELAND and EUKLID SAKELLARIOS (*Ber.*, 1919, **52**, [B], 898—904).—*Nitroethylene* can be prepared in 50% yield by the dehydration of β -nitroethyl alcohol by phosphoric oxide or sodium hydrogen sulphate; it is an almost colourless, mobile liquid, b. p. 98.5° , D_{15}^{25} 1.073, the vapour of which violently attacks the eyes and throat. It readily undergoes polymerisation; this occurs slowly when the pure substance is preserved, more rapidly on exposure to light. The process is remarkably catalysed by water, so that a freshly prepared aqueous solution of the substance becomes cloudy almost immediately, and the separation of the polymeride is complete in a few minutes (the substance cannot be depolymerised to nitroethylene by heat); polymerisation is retarded by acid, but in these circumstances a slow reaction with water occurs, with formation of β -nitroethyl alcohol. With alkali, polymerisation occurs with explosive violence. Reduction with stannous chloride and hydrochloric acid yields acetaldehyde and hydroxylamine, whilst with zinc dust and acetic acid ethylamine is produced. Nitroethylene unites immediately with bromine in ethereal solution, yielding *nitroethylene dibromide*, colourless liquid, b. p. $97^\circ/21$ mm., and with aniline giving *N- β -nitroethylaniline*, $\text{NHPh}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NO}_2$, colourless leaflets, m. p. 37° (the *hydrochloride* is described).

[With E. BLÜMICH].—Attempts to prepare nitroethylene by the elimination of hydrogen bromide from bromonitroethane by methylalcoholic potassium hydroxide were unsuccessful, the products being potassium bromide, potassium nitrite, and the *potassium salt* of dinitroethane, shining, golden needles which explode at about 150° ; *aa-dinitroethane* has b. p. $72^\circ/12$ mm.

H. W.

The Specific Gravity and Refractive Power of Solutions of Glycerol. H. WOLFF (*Zeitsch. angew. Chem.*, 1919, **32**, 1, 148).—The author has determined the density and refractive indices of solutions in water of an extremely pure sample of glycerol, with the following results:

86% *Solution*.— D_{15}^{15} 1.2294, n_D^{15} 1.4545, n_D^{15} 1.4537, n_D^{15} 1.4533; change in refractive index per $^\circ\text{C}$., 2.8×10^{-4} .

76.77% *Solution*.— D_{15}^{15} 1.2043, D_{15}^{15} 1.2036, D_{15}^{25} 1.1998, the coefficient of expansion being 0.000463. n_D^{15} 1.4401, n_D^{15} 1.43945, n_D^{15} 1.4388; change in refractive index per $^\circ\text{C}$ = 2.6×10^{-4} .

The results agree very closely with those contained in Gerlach's table, but not so closely with those of Lenz, Strohmer, and Skalweit, although there is fair agreement with the latter.

J. S. G. T.

New Initial Materials for the Preparation of Allyl Compounds. OSSIAN ASCHAN (*Finska Kem. Medd.*, 1918, 3 pp., from *Chem. Zentr.*, 1919, i, 221).—A mixture of glycerol and formic acid (95%) is heated for four hours under reflux in the presence of a small quantity of ammonium chloride as catalyst, and the product is fractionally distilled. At above 190°, the glycerol diformin primarily formed breaks down into allyl formate, water, and carbon dioxide, and decomposition is complete at 260°. Allyl chloride is obtained in good yield when cold allyl formate containing 10% of dissolved zinc chloride is treated with hydrogen chloride and the mixture is subsequently heated on the water-bath. H. W.

Action of Heat on the Alkali and Alkali-Earth Methyl Sulphates. J. GUYOT and L. J. SIMON (*Compt. rend.*, 1919, 168, 1054—1056).—Potassium methyl sulphate when heated at 220°, rising slowly to 280°, is decomposed almost quantitatively into potassium pyrosulphate and methyl ether. At a slightly lower temperature sodium methyl sulphate behaves similarly, but at the higher temperature 7% of the salt is decomposed into sodium sulphate and methyl sulphate. This second reaction with the formation of the two sulphates is the principal one, and occurs below 200° in the case of calcium, barium, and lithium methyl sulphates, and slowly in the cold in a desiccator in the case of strontium methyl sulphate. W. G.

Alcoholysis. AD. GRÜN, FRANZ WITTKA, and EMIL KUNZE (*Chem. Umschau Fett-Ind.*, 1917, 24, 15—16, 31—34; from *Chem. Zentr.*, 1919, i, 222—223).—The authors have investigated the direct conversion of fats into the ethyl esters of their fatty acids by boiling them with alcohol containing a small amount of mineral acid. Alcoholysis in an acid medium is found to be a consecutive process, thus showing that the hydrolysis of fats proceeds by separate steps in every case. Pure tristearin was obtained by the catalytic reduction of almond or sesame oil and removal of oleodistearin and free fatty acid by washing with light petroleum and boiling with alcohol. The best results were obtained when tristearin (100 parts) was heated for three hours with a 1% solution of sulphuric acid in absolute alcohol (150 parts). The product consisted of a mixture of mono-, di-, and tri-stearin and ethyl stearate, from which the tristearin could readily be removed by crystallisation from alcohol; the separation of the other components was effected after distillation of ethyl stearate under diminished pressure, and was best accomplished by a frequent change of solvent (alcohols in which monostearin is most readily, and light petroleum in which it is least readily, soluble). Three thousand grams of tristearin yielded 400 grams of unchanged material (after repeated alcoholysis of the fraction which had escaped action in the first treatment), 300 grams of distearin, 200 grams of monostearin, more than 1200 grams of ethyl stearate, and 600 grams of mixed frac-

tions. The distearin fraction had m. p. $74\cdot5^{\circ}$, 75° , $75\cdot5^{\circ}$ (it should be noted that a molar mixture of mono- and tri-stearin has the same m. p. as distearin); it was converted by thionyl chloride into distearochlorohydrin, m. p. 56° , described by Grün and Theimer, and appears to be the $\alpha\beta$ -distearin. The monostearin fraction was composed of indistinct crystals, m. p. 79 – 80° , hydroxyl number, 311·4. H. W.

Chemistry of the Glutaconic Acids. XI. The Occurrence of 1 : 3-Addition to the Normal Form. JOCELYN FIELD THORPE (T., 1919, 115, 679–686).

Lactonic Acids. BROR HOLMBERG (*Svensk. Kem. Tidskr.*, 1918, 30, 190–205, 215–222; from *Chem. Zentr.*, 1919, i, 223–224).—In extension of his work on the Walden inversion, the author has investigated the stereochemical and kinetic behaviour of lactonic acids. The hydrolysis of malic acid lactone has been examined from these points of view, and, since the behaviour of β -lactones differs in several respects from that of γ -lactones, the work has also been extended to paraconic acid.

r-Malic acid lactone, shining leaflets or thin plates, m. p. 64 – 65° , is prepared by the action of moist silver oxide on *r*-iodosuccinic acid; *d*-malic acid lactone, colourless syrup, $[\alpha]_D + 41^{\circ}$, in aqueous solution (2·5%), is similarly obtained from *l*-iodosuccinic acid. The rate of hydrolysis was measured by dissolving the crude acid in water or dilute nitric acid of the desired concentration and estimating the amount of lactone in the solution by heating a measured portion until hydrolysis was complete and determining the increase in acidity by titration. Autohydrolysis is a rather slow, unimolecular change; nitric acid somewhat increases the velocity of action. In acid solution, *d*-malic acid lactone yields a mixture of *r*- and *l*-malic acids, whilst almost pure *d*-malic acid is formed in alkaline solution.

The formation of paraconic acid by elimination of bromine from salts of itabromopyrotartaric acid is a unimolecular change which is not reversible in dilute solution. As acid salt and to a still greater extent as free acid, itabromopyrotartaric acid is only slowly converted into its lactone. Silver salts catalyse the elimination of bromine in acid solution. The formation of paraconic acid from itamalic acid is reversible. Acid salts of itamalic acid are only slowly converted into paraconic acid, and this is also true of the reverse action in neutral solution. Lactone formation and hydrolysis are catalysed by hydrogen ions. The affinity constants of itamalic acid and paraconic acid are approximately $K = 0\cdot0003$ – $0\cdot0004$. The hydrolysis of paraconic acid by alkali is a bimolecular reaction. H. W.

Action of Carbon Disulphide on Nitromethane. ERICH FREUND (*Ber.*, 1919, 52, [B], 542–544).—A mixture of nitromethane and carbon disulphide reacts with alcoholic potassium

hydroxide to give *potassium nitrodithioacetate*, as a brown, crystalline precipitate, decomp. 203.5° . When heated with potassium hydroxide, it yields potassium nitroacetate (Steinkopf, A., 1909, i, 559), and its solutions do not give an acid reaction until one equivalent of acid has been added, this change being interpreted as follows:



Some Metallic Derivatives of Ethyl Thioglycollate.

CHARLES A. ROULLER (*J. Amer. Chem. Soc.*, 1919, **41**, 777—781).—Ethyl thioglycollate was shown by Rowntree and Abel (*J. Pharmacol.*, 1910, **2**, 108) to dissolve antimonious and mercuric oxides, the hydrogen of the mercaptan group being completely replaced by the metal. The antimony derivative of the ester is an insoluble oil, but the corresponding amide is soluble in water and possesses trypanocidal properties. The author has found that the oxides of bismuth, copper, mercury, silver, zinc, tin, and arsenic react energetically with ethyl thioglycollate. It was hoped to prepare bactericidal substances, which would either be soluble in water or could be used in powder form on wound surfaces. *Triethyl bismuthtrithioglycollate*, $\text{Bi}(\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et})_3$, forms small, yellow crystals, m. p. $87-88^{\circ}$, soluble in alcohol. *Diethyl mercuridithioglycollate*, $\text{Hg}(\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et})_2$, long needles, m. p. 55° , is identical with the product obtained from mercuric chloride and two molecules of ethyl thioglycollate (Wislicenus, *Annalen*, 1868, **146**, 148). Ethyl silverthioglycollate, yellow needles from acetone, m. p. $75-77^{\circ}$, is with difficulty decomposed by concentrated nitric acid in sealed tubes. The action of silver nitrate on the ester was also investigated. With cupric hydroxide a crystalline substance is obtained which contains less than half the amount of copper to be expected from analogy with the previous reactions. It is very resistant to concentrated nitric acid at $200-270^{\circ}$. F. C.

Constitution of Maltose. A New Example of Degradation in the Sugar Group. JAMES COLQUHOUN IRVINE and JAMES SCOTT DICK (*T.*, 1919, **115**, 593—602).

Inversion of Sucrose by Mechanical Ionisation of Water. J. E. ABELOUS and J. ALOY (*Compt. rend.*, 1919, **168**, 1125—1128).—If 100 c.c. of a 5% solution of sucrose are passed five times through a Richardson pulveriser, 0.06 gram of invert sugar is obtained. The addition of sodium or potassium chloride appreciably increases the yield of invert sugar. Using a mixture of electrolytes such as is found in the Ringer-Locke solution, a slightly greater increase is obtained, and if a trace of zinc sulphate or, better still, a trace of zinc sulphate and a trace of manganese sulphate is added, the increase is still greater. On the other hand, the presence of a trace of potassium cyanide or of hydrocyanic

acid or of silver nitrate prevents the inversion taking place. The inversion is greater in Raulin's solution than in Locke's solution, and the authors have determined the effect of removing in turn each one of the ingredients of Raulin's solution in the inversion. The results so obtained are in agreement with those obtained by Raulin in his work on *Aspergillus niger*. Similarly, the anti-septics which inhibited the development of *Aspergillus niger* equally checked the inversion of sucrose. The curve showing the relationship between the amount of sucrose inverted and the number of passages through the pulveriser is sinusoidal, but slightly irregular.

W. G.

The Composition of Starch. I. Precipitation by Colloidal Iron. II. Precipitation by Iodine and Electrolytes. JOHN MELLANBY (*Biochem. J.*, 1919, **13**, 28—36).—When colloidal iron is added to a solution of starch three well-marked phases may be recognised; (i) a portion of the starch is precipitated by the colloidal iron only, (ii) a second portion of the starch is carried down with the colloidal iron when an electrolyte is added, and (iii) the filtrate from (ii) contains unprecipitated starch. Eighty % of the starch is precipitated in the first phase, independently of the amount of iron added. Starch in solution bears a negative charge. From these observations it is concluded that amylogranulose may be divided into three fractions, α , β , and γ , according to their precipitability by colloidal iron.

Quantitative studies of the reaction between starch and iodine indicate that a quantitative reaction takes place between the starch and the ionised iodine. The theory that iodine reacts chemically with starch is strengthened by the fact that the equivalent point is not affected by dilution, temperature, or the precipitating electrolyte. On this basis the least value for n for $(C_6H_{10}O_5)_n$ is 10, assuming that one molecule of starch reacts with one atom of iodine. This value is, of course, only a mean value for a number of starch complexes, such as α , β , and γ granulose, in which n is continually varying. For amylogranulose γ (unprecipitated by colloidal iron), $(C_6H_{10}O_5)_5$ is equivalent to I. After the formation of the starch iodide it may adsorb further quantities of iodine, depending on the iodine concentration of the original mixture.

J. C. D.

The Supposed Degradation of Starch by Formaldehyde. MARTIN JACOBY (*Ber.*, 1919, **52**, [B], 558—562).—Woker's assumption that formaldehyde resembles diastase in its action on starch is primarily based on the fact that mixtures of starch and formaldehyde soon lose the power of giving a blue colour with iodine (*A.*, 1917, i, 61, 447). It is now shown that the addition of ammonium acetate is quite sufficient to restore this power, whereas it has no influence on the iodine reaction with starch which has been left with diastase (compare also von Kaufmanh, *ibid.*, 251).

J. C. W.

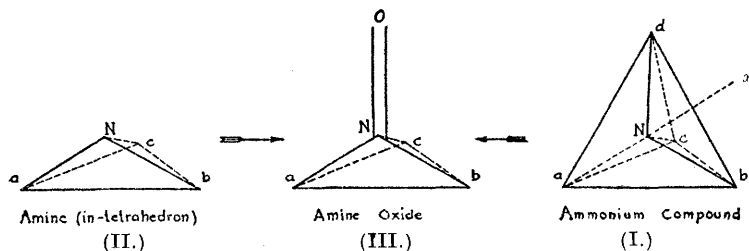
The Nature of Solutions of Starch in Formalin, and the Quantitative Re-conversion of Formalin-Starch into Starch. The Colour of Iodine Solutions. W. VON KAUFMANN and A. LEWITE (*Ber.*, 1919, **52**, [B], 616—627. Compare A., 1917, i, 251).—The fact that solutions of starch and formalin merely contain an additive compound of the two agents and not hydrolytic products as Woker supposed, is proved by the quantitative recovery of absolutely unchanged starch from such mixtures by precipitation with alcohol.

The colorations with iodine which such solutions produce (resembling those given by partly hydrolysed starch) may be explained in the terms of colloid chemistry. If, as Harrison assumes (*Zeitsch. Chem. Ind. Kolloide*, 1911, **9**, 5), the well-known blue colour is the colour of colloidal iodine protected by the starch, then formaldehyde causes a reversible increase in the degree of dispersion, and the addition of electrolytes an aggregation of the particles (the blue colour is restored by electrolytes), which is furthermore hindered by the addition of a protective colloid like gum-arabic.

The colour of iodine solutions in halogen derivatives of methane and ethane changes from brown to violet according as the number of un-substituted hydrogen atoms falls. J. C. W.

Space Representation of Organic Nitrogen Compounds.

PANCHANAN NEOGI (*J. Amer. Chem. Soc.*, 1919, **41**, 622—639).—A theoretical paper, in which it is shown that the properties of nitrogen compounds can only be explained on the assumption of a tetrahedral formula for nitrogen, using the complete figure for quinquivalent nitrogen (I) and the "inner tetrahedron" for tervalent nitrogen (II), thus:



The subjects discussed are as follows. (1) The non-equivalence of the fifth bond, as revealed by the discovery of isomerides of the type $(\text{NMe}_3 \cdot \text{OR})\text{OR}'$ and $(\text{NMe}_3 \cdot \text{OR}')\text{OR}$ (Meisenheimer, A., 1913, i, 595). (2) The non-existence of any isomerides of the types Na_3bx and Na_2bcx , and the existence of only two optical isomerides of the type Nabcdx . (3) The existence of only four optical isomerides in the case of compounds containing one asymmetric carbon

and one asymmetric nitrogen, or two asymmetric nitrogen atoms. (4) The non-existence of isomeric pyridinium and quinolinium compounds and the existence of isomeric tetrahydroquinolinium salts. (5) The failure to resolve amines of the type *Nabc* into optical isomerides has hindered the general acceptance of a space representation for trivalent nitrogen, although the above formula is used to explain the isomerism of the oximes, etc. It also explains why *tert.*-amines of this type give enantiomorphous amine-oxides on oxidation (Meisenheimer, A., 1912, i, 25), these compounds being represented as in (III) above. J. C. W.

Preparation of Diacetoneamine. ARTHUR ERNEST EVEREST (T., 1919, 115, 588—592).

The Mechanism of the Artificial Formation of Carbamide by Oxidation, and the Synthesis of the Natural Principals in Plants. R. FOSSE (*Compt. rend.*, 1919, 168, 1164—1166. Compare this vol., i, 297).—The oxidation of very small amounts of dextrose in strong ammonium hydroxide solution gives rise to considerable proportions of cyanic acid and carbamide. After tautomerisation of the ammonium cyanate by heat the yield of carbamide exceeds 70% of the dextrose used. Much higher yields of carbamide are obtained by oxidising, under the same experimental conditions, formaldehyde or urotropine. The author suggests that in the formation of carbamide from sugars by oxidation, formaldehyde is first formed, and is then converted by the action of ammonia and oxygen into hydrogen cyanide, which is further oxidised to cyanic acid, which with ammonia yields carbamide. W. G.

Certain Metallo - Ferrocyanide Compounds, their Behaviour towards Chlorine and Bromine, and their Use in Analysis. FRANZ FELIX WERNER (*Zeitsch. anal. Chem.*, 1919, 58, 23—24. Compare A., 1912, ii, 687).—*Manganese ferrocyanide*.—A white substance which is coloured green by chlorine water and oxidised to the brown ferricyanide by bromine water. *Nickel ferrocyanide*.—Bluish-green; not attacked by chlorine water, but converted into the brown ferricyanide by bromine water. *Cobalt ferrocyanide*.—An unstable, green compound, which chlorine water oxidises to the ferricyanide; it is decomposed by bromine water, yielding black, hydrated cobalt oxide. *Mercurous ferrocyanide*.—The grey compound is coloured green when treated with chlorine water or bromine water. *Mercuric ferrocyanide*.—White; chlorine water colours it green and bromine water brown. *Bismuth ferrocyanide*.—A yellowish-green compound which is not attacked by chlorine water or bromine water. [See further, *J. Soc. Chem. Ind.*, 1919, July.] W. P. S.

The Benzene Problem. A. VON WEINBERG (*Ber.*, 1919, 52, [B], 928—940).—A theoretical paper, in which the author advances an explanation of the atomic structure of benzene based on the continuous oscillation of the atoms within the molecule. The author considers that in the case of the double bond two valencies of one atom saturate or strive to saturate two valencies of a neighbouring atom in consequence of the oscillation of the atomic nuclei; a considerable amount of evidence in favour of this hypothesis is deduced from consideration of the internal energy, molecular volume, absorption spectra, intramolecular change, and Walden inversion of substances containing unsaturated groups and of the influence of double bonds on the stability of the molecule. The argument is extended to conjugated linkings and thence to benzene; in the latter case the six carbon atoms only lie in one plane as a transitory phase; otherwise, the atoms 1, 3, 5 and the atoms 2, 4, and 6 are on opposite sides of the plane. The oscillation model is shown to account satisfactorily for the phenomena of substitution and to allow the construction of symmetrical formulæ for naphthalene, anthracene, phenanthrene, and pyrene, whilst it also accounts for the difference in properties between benzene and *cyclooctatetraene*; it leads to a uniform formulation of *p*-quinones and quinols, and accounts for the existence of two forms of *o*-quinones. Triphenylmethyl and the metallic ketyls can be formulated without recourse to tervalent carbon, whilst the phenomena of hydrogenation of the phthalic acids are also explained. For details, the original paper must be consulted. H. W.

The Melting Points, Refractive Indices and Densities of a Series of Dihalogenobenzenes. J. NARBUTT (*Ber.*, 1919, 52, [B], 1028—1034).—The melting points were determined by observation of the cooling curves of the molten substances, and are accurate to within $\pm 0.02^\circ$ for m. p.'s above the atmospheric temperature and to within $\pm 0.1^\circ$ for those of lower temperature; the error in the case of the refractive indices, determined with an Abbé refractometer, does not exceed $\pm 0.0002-3$, whilst the densities are accurate to $\pm 0.0001-2$. The following constants have been determined: *p*-dichlorobenzene, m. p. 52.9° ; *o*-dichlorobenzene, m. p. -17.5° , D_4^{15} 1.3104, $D_4^{20.4}$ 1.3048, n_D^{17} 1.5524; *m*-dichlorobenzene, m. p. -24.4° , D_4^{15} 1.2937, D_4^{20} 1.2881, $n_D^{17.3}$ 1.5472; *p*-chlorobromobenzene, m. p. 64.6° ; *o*-chlorobromobenzene, m. p. -12.6° , D_4^{15} 1.6511, D_4^{20} 1.6444, $n_D^{17.3}$ 1.5821; *m*-chlorobromobenzene, m. p. -21.2° , D_4^{15} 1.6365, D_4^{20} 1.6297, $n_D^{17.1}$ 1.5773; *p*-dibromobenzene, m. p. 86.9° ; *o*-dibromobenzene, m. p. $+1.8^\circ$, D_4^{15} 1.9633, D_4^{20} 1.9557, $n_D^{17.4}$ 1.6117; *m*-dibromobenzene, m. p. -6.9° , D_4^{15} 1.9599, D_4^{20} 1.9523, $n_D^{17.4}$ 1.6083; *p*-bromoiodobenzene, m. p. 90.1° ; *o*-bromoiodobenzene, m. p. $+2.1^\circ$; *m*-bromoiodobenzene, m. p. -9.3° ; *p*-diiodobenzene, m. p. 129.0° ; *o*-diiodobenzene, m. p. 23.4° ; *m*-diiodobenzene, m. p. 34.2° . H. W.

Products of Nitration of *p*-Cymene. OSSIAN ASCHAN [with TERÄSVUORI and PER EKWALL] (*Finska Kem. Medd.*, 1918, 5 pp.; from *Chem. Zentr.*, 1919, i, 227).—Direct nitration of cymene

yielded 2-nitrocymene, D_4^{20} 1.067, in minimal amount. Cymene was also gradually added to well-cooled concentrated nitric acid (D 1.52), and the following substances were isolated by prolonged fractional crystallisation of the solidified product. I. *Substance*, $C_{18}H_{17}O_{10}N_5$, yellow needles, m. p. 70° , which when reduced with ammonium sulphide yielded an *amine*, orange needles, m. p. $77-78^\circ$ (*hydrochloride*, m. p. $215-218^\circ$). II. 3:5-Dinitro-*p*-cymene, greenish-white plates, m. p. 54° , which were reduced to *nitrocarvacrylamine*, yellow needles or prisms, m. p. $80-82^\circ$ (*hydrochloride*, pale red crystals, m. p. $208-210^\circ$; *acetyl* derivative, m. p. 111°). *Nitrocarvacrol*, needles, m. p. $116-117^\circ$, was formed as by-product during diazotisation. III. *Substance*, $C_{10}H_{12}O_5N_2$, probably dinitrohydroxy-*p*-cymene, $C_6H_2Me(NO_2)_2 \cdot CMe_2 \cdot OH$, prisms or plates, m. p. $90-91^\circ$. H. W.

The Dimethylnaphthalenes of Coal Tar. R. WEISSGERBER and O. KRUBER (*Ber.*, 1919, **52**, [B], 346—370).—Physical methods for the separation of the dimethylnaphthalenes in the heavy-oil fraction, b. p. $260-265^\circ$, seem to be out of the question, and when it is considered how many sulphonic acids could be formed by the ten possible isomerides, no great help could be expected from the sulphonation method which has served so well in the case of the polymethylbenzenes. Nevertheless, the authors have tried the method, and by varying the conditions have succeeded in isolating the 1:6-, 2:6-, and 2:7-isomerides with far less trouble than was anticipated.

1:6-DIMETHYLNAPHTHALENE.—The crude oil is purified by alternate fractionation and agitation with small quantities of concentrated sulphuric acid in the cold. It is then stirred with 60% of its weight of 98% sulphuric acid for eight to ten hours at about 40° , when the pasty mass of sulphonic acids is separated and mixed with a little water. A solid *sulphonic acid* is deposited, which is purified by crystallisation from 33% sulphuric acid and converted into its *sodium* salt, bundles of needles, $1H_2O$, and *amide*, $C_{12}H_{13}O_2NS$, m. p. 185° . The sulphonic acid is hydrolysed by means of steam at $130-140^\circ$ to 1:6-dimethylnaphthalene, which has b. p. $262-263^\circ$, D^{15} 1.0056 (α -methylnaphthalene has $D^{11.5}$ 1.0267), and forms a *picrate*, long, orange-red needles, m. p. 114° . The constitution of the hydrocarbon is revealed by the following series of reactions.

By the alkaline fusion of the sulphonate, 4:7-dimethyl- α -naphthol is obtained, in slender needles, m. p. 82° , which couples with benzenediazonium chloride to form a *dye*, $C_{18}H_{16}ON_2$, dark red leaflets, m. p. 134° , which is insoluble in, and indifferent to, potassium hydroxide, and is therefore an *o*-hydroxyazo-compound. On oxidation with chromic acid in glacial acetic acid, the hydrocarbon yields 2:5-dimethyl- α -naphthaquinone, which crystallises in pale yellow rosettes of pungent-smelling needles, m. p. 95° , and may be oxidised further, by permanganate, to 3-methyl-*o*-phthalic acid (Jürgens, A., 1907, i, 1036). The production of the *o*-azo-dye, the

p-quinone, and the 3-methylphthalic acid indicates that the hydrocarbon is either a 1:6- or 1:7-dimethylnaphthalene and the sulphonic acid the 4-derivative. For the final decision, oxidation to a dicarboxylic acid is necessary, but many methods were tried before this could be accomplished. Oxidation with alkaline ferricyanide gives *naphthalene-1:6-dicarboxylic acid*, which crystallises in microscopic needles, m. p. 310°, and forms a *methyl* ester, rosettes of needles, m. p. 99°. Prolonged boiling with about 5% nitric acid, however, gives chiefly *6-methyl- α -naphthoic acid*, which crystallises in slender, white needles, m. p. 150—152°, forms a *methyl* ester, a pale yellow oil with a resinous odour, b. p. 183—187°/30 mm., and an *ethyl* ester, b. p. 203—205°/30 mm., and yields β -methyl-naphthalene when heated with hydrochloric acid at 222—230°.

The above dicarboxylic acid was also prepared as follows: β -Naphthylamine-5-sulphonic acid is diazotised and boiled with cuprous cyanide, the *potassium 6-cyanonaphthalene-1-sulphonate* is distilled with potassium cyanide, and the 1:6-dicyanonaphthalene (short needles, m. p. 208—210°; compare Darmstädter and Wichelhaus, *Annalen*, 1869, **152**, 309) is hydrolysed.

2:6-DIMETHYLNAPHTHALENE.—If the sulphonation is carried out at 135—140°, and the product is poured on ice, a much less soluble *sulphonic acid* soon crystallises. This crystallises in large, glistening leaflets, gives a sparingly soluble *sodium* salt, $5\text{H}_2\text{O}$, and an *amide*, m. p. 265—266°, and yields the known 2:6-dimethylnaphthalene on hydrolysis. The hydrocarbon has m. p. 110—111°, b. p. 261—262°, and has the odour of aniseed, whereas the specimen obtained by Baeyer and Villiger from ionone (A., 1899, i, 922) had the odour of orange blossom. The identity of the compound is established, however, by its oxidation with chromic acid to 2:6-dimethylnaphtha-1:4-quinone and then by permanganate to trimellitic acid (*ibid.*).

The explanation of the different course of the sulphonation was found by sulphonating the pure hydrocarbons. 1:6-Dimethylnaphthalene yields the 4-sulphonic acid in the cold, but a mixture of freely soluble acids at above 100°; 2:6-dimethylnaphthalene yields the freely soluble 8-sulphonic acid in the cold, which is hydrolysed to the hydrocarbon by boiling with about 70% sulphuric acid, and converted into the 7-sulphonic acid by heating with 78% sulphuric acid at 135—140°. The constitution of the sulphonic acids follows from the properties of the corresponding naphthols. 2:6-Dimethylnaphthalene-8-sulphonic acid [*3:7-dimethyl- α -naphthalenesulphonic acid*] crystallises in flat needles and tablets, its *chloride* in stout prisms, m. p. 105—107°, and its *amide* in rosettes of leaflets, m. p. 207°. The product of the alkaline fusion, 3:7-dimethyl- α -naphthol, forms colourless needles, m. p. 105—106°, and couples with benzenediazonium chloride to give *bisbenzeneazo-3:7-dimethyl- α -naphthol*, $\text{C}_{24}\text{H}_{20}\text{ON}_4$, in steel-blue needles, m. p. 191°. 3:7-Dimethyl- β -naphthalenesulphonic acid, the above product of the sulphonation at 135—140°, gives rise to 3:7-dimethyl- β -naphthol, which crystallises in glistening needles, m. p. 173—174°.

and forms a *benzeneazo*-compound, in brilliant orange-red needles, m. p. 149—151°. This is converted into 3:7-*dimethylnaphtha*-1:2-*quinone*, ruby-red needles, m. p. 151—152°, by reduction to the aminonaphthol, followed by oxidation with dichromate. 2:6-Dimethylnaphtha-1:4-*quinone* (above) reacts with phenylhydrazine to form 4-*benzeneazo*-2:6-*dimethyl- α -naphthol*, which crystallises in fiery orange-red needles, m. p. 240—241° (decomp.), and changes in alcoholic solution from orange to magenta on the addition of alkali hydroxide.

2:7-DIMETHYLNAPHTHALENE.—For practical purposes, it is not advisable to isolate the 2:6-isomeride from the original oil, but to proceed as follows: the oil is sulphonated in the cold, and the liquid sulphonic acids removed from the solid 1:6-dimethylnaphthalenesulphonic acid are heated at 150—160° for a few hours and then hydrolysed, giving a mixture of solid and liquid hydrocarbons. The solid mixture generally has m. p. 50—60°, but is frequently so rich in the 2:6-isomeride as to yield this readily by fractional crystallisation. If not, it is sulphonated at 135—140°, the solid 2:6-dimethylnaphthalenesulphonic acid is removed, and the liquid acids hydrolysed again. Once more a mixture of solid hydrocarbons with low m. p. is obtained. This is then sulphonated at about 40°, and the pasty product crystallised from 30% sulphuric acid. Two sulphonic acids separate, which are hydrolysed in the usual way, when 2:7-*dimethylnaphthalene* is obtained in glistening leaflets with an aromatic odour, m. p. 96—97°, b. p. 262°, the *picrate* crystallising in pale yellow needles, m. p. 135—136°.

The constitution of the new hydrocarbon is established in the usual way. When sulphonated at 100°, it yields 2:7-*dimethylnaphthalene*-3-sulphonic acid, which crystallises in pearly, sword-like forms, and forms a *sodium* salt, bundles of needles, and an *amide*, m. p. 197—198°. The sodium salt can also be isolated from the above crude mixture obtained by sulphonating in the cold, or from the mother liquors of the above 2:6-dimethylnaphthalenesulphonate. When fused with potassium hydroxide, the salt yields 3:6-*dimethyl- β -naphthol*, in lanceolate crystals, m. p. 171—172°, which gives a brilliant orange-red *benzeneazo*-dye, m. p. 183—184°. When the dye is reduced and the white amine is oxidised by chromic acid, 3:6-*dimethylnaphtha*-1:2-*quinone* is obtained, in stout, brownish-red prisms, m. p. 152—153°. The isomeric 3:6-*dimethylnaphtha*-1:4-*quinone*, yellow needles, m. p. 114—115°, is obtained by oxidising the hydrocarbon with chromic acid, and it yields trimellitic acid on oxidation with permanganate.

The coal-tar fraction, b. p. 220—290°, is commonly regarded as being poor in solid ingredients, in fact, is often used to maintain other fractions in the liquid state. The discovery of two solid dimethylnaphthalenes is therefore contrary to this idea. The only genuine oils in the fraction are the β -methyl- and 1:6-dimethylnaphthalenes, the fluidity being due to the enormous depression of the freezing point mutually exerted by the ingredients. A

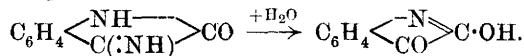
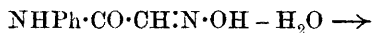
possible outlet for naphthalene as an oil would therefore consist in methylating it. J. C. W.

2:3-Dimethylnaphthalene in Coal Tar. R. WEISSGERBER (*Ber.*, 1919, **52**, [B], 370—371).—On working up the liquid sulphonic acids accompanying the 2:6-dimethylnaphthalene-sulphonic acid (preceding abstract), a well-defined sodium salt was once accidentally obtained which gave a fourth dimethylnaphthalene, crystallising in large leaflets, m. p. 104—105°. By direct comparison, this has now been identified with the 2:3-dimethylnaphthalene (guaiene) recently obtained by Schroeter and others from guaiacum resin (this vol., i, 84). J. C. W.

Oximinoacetanilides and their Condensation to Isatins.

T. SANDMEYER (*Helv. Chim. Acta*, 1919, **2**, 234—242).—If a freshly prepared solution of hydroxylamine sulphate is boiled with aniline or many of its derivatives and chloral hydrate, oximinoacetanilides are formed, according to the equations: $\text{CCl}_3\cdot\text{CHO} + \text{NH}_2\cdot\text{OH} \rightarrow \text{CCl}_3\cdot\text{CH:N}\cdot\text{OH}$; this
 $+ \text{NH}_2\text{Ph} + \text{H}_2\text{O} = \text{NHPh}\cdot\text{CO}\cdot\text{CH:N}\cdot\text{OH}$.

The majority of these compounds, if the ortho-position is unoccupied, give excellent yields of isatins when heated with sulphuric acid at temperatures varying from 55° to 100° and then diluted with water; thus:



The solution of hydroxylamine sulphate is obtained by boiling one of hydroxylaminesulphonic acid, prepared by Raschig's method. The oximinoacetanilides are all more or less pale yellow, flocculent, crystalline precipitates. The following have been prepared: *oximinoacet-anilide*, m. p. 175°; -o-, -m-, and -p-*toluidides*, m. p.'s 121°, 146°, 162° respectively; -m- and -p-*xylydides*, m. p.'s 161° and 151°; -o-*anisidide*, m. p. 140°; -p-*phenetidide*, m. p. 195°; -*methyl*-, -*ethyl*-, and -*benzyl-anilides*, m. p.'s 145°, 160°, and 142°; -o-, -m-, and -p-*chloroanilides*, m. p.'s 150°, 154°, 165°; -2:5-, -3:4-, and -3:5-*dichloroanilides*, m. p.'s 163°, 158°, 185°; -5- and -4-*chloro-o-toluidides*, m. p.'s 167°, 148°; -6- and -4-*chloro-m-toluidides*, m. p.'s 187°, 134°; -2- and -3-*chloro-p-toluidides*, m. p.'s 177°, 188°; -4-*chloro-o-anisidide*, m. p. 182°; -p-*bromoanilide*, m. p. 167°; -2:4-*dibromoanilide*, m. p. 215°; and *oximinoacetanthranilic acid*, m. p. 208°.

The following isatins are new: 4:7-*dimethylisatin*, orange-yellow, m. p. 250°; 7-*chloroisatin*, reddish-brown, m. p. 175°; 4:6-*dichloroisatin*, lemon-yellow, m. p. 250°; 4-*chloro-7-methylisatin*, orange-yellow, m. p. 273°; 5-*chloro-7-methylisatin*, yellowish-brown, m. p. 265°; 7-*chloro-4-methylisatin*, orange-yellow, m. p. 252°; 4-*chloro-7-methoxyisatin*, dark red, m. p. 240°; and *isatin-7-carboxylic acid*, brownish-yellow, m. p. 235°. J. C. W.

The Conception of Internal Molecular Strain and the Theory of Benzene. D. VORLÄNDER (*Ber.*, 1919, 52, [B], 263—283).—A theoretical paper dealing chiefly with the problems of orientation in the benzene series.

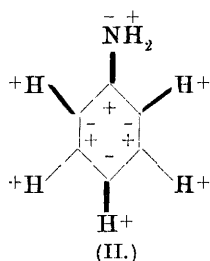
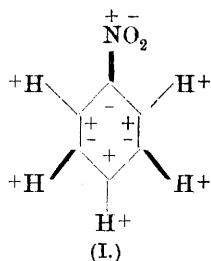
I. Positive and Negative Radicles attached to the Benzene Nucleus.—The various radicles are sharply divided into two classes, according to the position occupied by the second substituent in bromination, nitration, or sulphonation. One group exerts a *positive* influence, directing the new substituent into the *meta*-position, and includes $\cdot\text{SO}_3\text{H}$, $\cdot\text{NO}_2$, $\cdot\text{CHO}$, $\cdot\text{CH}\cdot\text{NO}_2\text{H}$, $\cdot\text{CO}_2\text{H}$, $\cdot\text{CO}_2\text{Alk}$, $\cdot\text{CO}\cdot\text{NH}_2$, $\cdot\text{COAlk}$, $\cdot\text{CO}\cdot\text{CO}_2\text{H}$, $\cdot\text{C}\cdot\text{OH}$, $\cdot\text{CN}$, $\cdot\text{CCl}_3$, $\cdot\text{NH}_3\text{X}$, $\cdot\text{NH}_2\text{Alk}\cdot\text{X}$, $\cdot\text{NHAlk}_2\text{X}$, $\cdot\text{NAlk}_3\text{X}$, $\cdot\text{NH}_2\text{AcylX}$. The other group has a *negative* influence, and is *ortho-para* orienting; it includes halogens, $\cdot\text{OH}$, $\cdot\text{OAlk}$, $\cdot\text{OAcyl}$, $\cdot\text{NH}_2$, $\cdot\text{NHAlk}$, $\cdot\text{NAlk}_2$, $\cdot\text{NHAcyl}$, $\cdot\text{N}\cdot\text{N}\cdot$, $\cdot\text{CH}_3$, $\cdot\text{CH}_2\text{Alk}$, $\cdot\text{CHAlk}_2$, $\cdot\text{CMe}_3$, $\cdot\text{CH}_2\text{Cl}$, $\cdot\text{CH}_2\cdot\text{O}\cdot\text{NO}_2$, $\cdot\text{CH}_2\cdot\text{SO}_3\text{H}$, $\cdot\text{CH}_2\cdot\text{NH}_2$, $\cdot\text{CH}_2\cdot\text{CN}$, $\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, $\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, $\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, $\cdot\text{CH}\cdot\text{CH}\cdot\text{NO}_2$, $\cdot\text{C}\cdot\text{C}\cdot\text{CO}_2\text{H}$, $\cdot\text{C}_6\text{H}_5$. At first sight, it would seem to be a novel conception to regard the groups $\cdot\text{SO}_3\text{H}$, $\cdot\text{CO}_2\text{H}$, and $\cdot\text{NR}_3\text{X}$ as positive and $\cdot\text{NH}_2$ as negative, and to find a difference between $\cdot\text{COMe}$ on the one hand and $\cdot\text{OMe}$ and $\cdot\text{CH}_3$ on the other, but the author's notion is not based on any valency theories at all. The terms + and – are used to express the kind of antithesis or strain between the connected atoms. Thus, in any member of the above positive series, the atom which is attached to the benzene ring is positive; for example, $\text{Ph}\cdot\overset{+}{\text{NR}_3}\cdot\overset{-}{\text{OH}}$, $\text{Ph}\cdot\overset{+}{\text{NO}_2}$, $\text{Ph}\cdot\overset{+}{\text{COR}}$, $\text{Ph}\cdot\overset{+}{\text{SO}_2}\cdot\overset{-}{\text{OH}}$, $\text{Ph}\cdot\overset{+}{\text{CO}}\cdot\overset{+}{\text{OH}}$. In the negative series, the connecting atom is negative, thus: $\text{Ph}\cdot\overset{-}{\text{OCH}_3}$, $\text{Ph}\cdot\overset{-}{\text{CH}_3}$, $\text{Ph}\cdot\overset{-}{\text{NH}_2}$, $\text{Ph}\cdot\overset{-}{\text{OH}}$.

II. The Nature of the Ammonium Salt Group, $\cdot\text{NR}_3\text{X}$.—In the following abstract it is shown that aromatic quaternary ammonium salts are difficult to brominate or nitrate, but that the second substituent goes to the *meta*-position. The group $\cdot\text{NR}_3\text{X}$ therefore resembles the $\cdot\text{NO}_2$ group. This is interesting in view of the fact that anilines and their alkyl and acyl derivatives, which give *ortho*- and *para*-derivatives when brominated or nitrated in acetic acid solution, yield *meta*-compounds if dissolved in an excess of concentrated sulphuric acid, for then they are acting as ammonium salts. Like the $\cdot\text{CO}$, $\cdot\text{NO}_2$, and $\cdot\text{CN}$ groups, also, the $\cdot\text{NR}_3\text{X}$ group protects the benzene nucleus against oxidation and coupling; for example, when *o*-tolyltrimethylammonium sulphate is oxidised, it merely gives *o*-benzobetaine (this vol., i, 262). Unlike these groups, however, the $\cdot\text{NR}_3\text{X}$ radicle has no chromophoric properties, in spite of the fact that the production of perbromides, etc., shows it to be somewhat unsaturated.

III. Nitration of Benzotrichloride and tert.-Butylbenzene.—Under conditions which preclude the hydrolysis of benzotrichloride, nitration gives a *meta*-compound (this vol., i, 263). This illustrates the difference between the $\cdot\text{CH}_3$ group, in which the

carbon is $-$, and the $\cdot\text{CCl}_3$ group, in which it is $+$ *tert.*-Butylbenzene, on the other hand, gives almost entirely a *p*-nitro-derivative (this vol., i, 261). It is very difficult to chlorinate or oxidise, there being apparently a steric hindrance against the occupation of the ortho-position.

IV. *The Benzene Theory* (compare A., 1902, ii, 250).—The carbon atoms in the benzene ring are also written alternately $+$ and $-$. If the ring bears a positive substituent like $\cdot\text{NO}_2$, the formula may be expressed as in (I), if a negative substituent like $\cdot\text{NH}_2$, as in (II), in which the strong lines represent greater, and the weak lines lesser, tensions.



This conception helps to explain why compounds of the first type are more stable than the others, and why the first give meta-derivatives with halogen or nitric and sulphuric acids, whilst the second give ortho- and para-compounds. Other problems are discussed along the same lines, including the position occupied by a third substituent when (a) two positive, (b) two negative, and (c) one positive and one negative substituents are already present.

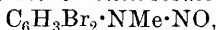
J. C. W.

Bromination and Nitration of Aromatic Quaternary Ammonium Salts. D. VORLÄNDER and ERNST SIEBERT (*Ber.*, 1919, 52, [B], 283—307).—I. *Bromination of Phenyltrimethylammonium Bromide*.—This salt is prepared as follows: dimethylaniline is warmed with methyl sulphate and benzene, the hygroscopic product, $\text{NMe}_3\text{Ph}\cdot\text{SO}_4\text{Me}$, m. p. $71-92^\circ$ (Ullmann, A., 1903, i, 394), is dissolved in 20% hydrobromic acid and treated with bromine, and the tribromide so formed (Tafel, A., 1898, i, 519) is boiled with water and the solution evaporated. Phenyltrimethylammonium bromide forms colourless crystals, m. p. 214° , and the corresponding picrate has m. p. 115° . Tafel did not succeed in brominating the salt (A., 1898, i, 471), but it is now found that reaction with bromine takes place at 70° in the presence of iron powder, the product being *m*-bromophenyltrimethylammonium bromide, $\text{C}_6\text{H}_4\text{Br}\cdot\text{NMe}_3\text{Br}$. This crystallises in stout prisms, m. p. $236-238^\circ$ (decomp.), combines with bromine to form an orange-red tribromide, m. p. $93-95^\circ$, and a yellow dibromide, m. p. $120-122^\circ$, and may be converted into the corresponding iodide, colourless prisms, m. p. 202° (Wurster and Scheibe, A., 1879,

107), *tri-iodide*, dark brown leaflets, m. p. 110°, and yellow *picrate*, m. p. 151°. The iodide decomposes at 165°/13 mm. into *m*-bromodimethylaniline (*ibid.*), which has m. p. 9—10°, b. p. 125°/10 mm., 253—254°/atm., and is characterised by its *picrate*, hexagonal tablets or prisms, m. p. 134—138°, and by conversion into *m*-bromo-*p*-nitrosodimethylaniline, brownish-green needles, m. p. 116° (not 148° as given by Wurster and Scheibe).

If the bromination is carried out at 100—120°, the product is 3:4-dibromophenyltrimethylammonium bromide, which crystallises as a mass of minute filaments, m. p. 180° (decomp.). The corresponding *tribromide*, $C_6H_3Br_3 \cdot NMe_3 \cdot Br_3$, forms golden-yellow leaflets, m. p. 147—149° (decomp.); the *iodide* crystallises in almost white, glistening needles, m. p. 185° (decomp.), and the *tri-iodide* forms brown leaflets, m. p. 136—138°. If the iodide is converted into the hydroxide, and this is distilled under reduced pressure, 3:4-dibromodimethylaniline is formed. This crystallises in needles or hexagonal tablets, m. p. 68—70°, decomposes into a reddish-violet dye on distillation under ordinary pressures, and may also be obtained by brominating 3-bromodimethylaniline or methylating 3:4-dibromoaniline. The base forms a characteristic *picrate*, flat, yellow needles, m. p. 142—146°, and a *perbromide*, m. p. 161—163° (decomp.), yields a mixture of products when treated with nitrous acid, including a golden-yellow *nitro*-compound, m. p. 131°, and may be converted into the above 3:4-dibromophenyltrimethylammonium salts after treatment with methyl sulphate.

For the sake of comparison, the unknown 3:5- and 3:6-dibromodimethylanilines have been prepared from the corresponding anilines by means of methyl sulphate. 3:5-Dibromodimethylaniline crystallises in large, white tablets, m. p. 77—79°, and forms a *picrate*, m. p. 151—153°, and 3:5-dibromophenyltrimethylammonium tribromide may be precipitated by means of bromine and hydrobromic acid from the alkaline mother liquor obtained in the preparation as yellow leaflets, m. p. 149° (decomp.). 3:6-Dibromodimethylaniline has m. p. below -35°, b. p. 134—137°/10 mm., forms a pale yellow *picrate*, m. p. 149°, and reacts with nitrous acid to give 3:6-dibromonitrosomethylaniline,



in small, white needles, m. p. 86—87°. 3:6-Dibromophenyltrimethylammonium tribromide forms golden-yellow leaflets, m. p. 135—136° (decomp.).

II. *Nitration of Phenyltrimethylammonium Nitrate*.—The bromide is converted into the nitrate, m. p. 110—115°, by evaporating two or three times with dilute nitric acid. Nitration takes place when the salt is heated at 100° with fuming nitric acid for eight hours, the product being *m*-nitrophenyltrimethylammonium nitrate, which crystallises in colourless prisms, m. p. 220—240° (decomp.) (compare Tafel, *loc. cit.*). The corresponding *picrate* forms yellow tablets, m. p. 151—153°, the *iodide* hexagonal or quadratic tablets, decomp. 205°, and the *tri-iodide* dark brown

leaflets, m. p. 143—145° (decomp.). The iodide yields *m*-nitrodimethylaniline, m. p. 58—60°, when heated in a vacuum, the product being identical with one made by Ullmann's method (A., 1900, i, 619). The action of sodium nitrite on hydrochloric acid solutions of this base leads to different products, according to the concentration of the acid. In dilute acid, the product is *m*-nitro-nitrosomethylaniline, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NMe} \cdot \text{NO}$, m. p. 76° (Noelting and Stricker, A., 1886, 544); from more concentrated solutions (acid with D 1.1—1.2), the products also include 3:4- and 3:6-dinitrodimethylanilines, m. p.'s 174—175° and 112° respectively.

III. *Nitration of o-Tolyltrimethylammonium Nitrate*.—Dimethyl-*o*-toluidine is methylated by means of methyl sulphate, the product is converted into the ammonium tribromide, and this is heated with dilute nitric acid. *o-Tolyltrimethylammonium nitrate* crystallises in quadratic leaflets, m. p. 175°; the corresponding *picrate* has m. p. 112—114°, the *mercurichloride* m. p. 192° (decomp.), and the *aurichloride* m. p. 189°. The nitrate readily reacts with boiling nitric acid (D 1.51) to form 5-nitro-*o*-tolyltrimethylammonium nitrate, $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NMe}_3 \cdot \text{NO}_3$, in flat needles, m. p. 230—235° (decomp.), which behave in a remarkable manner towards alkalis. When covered with 33% potassium hydroxide, the salt becomes bluish-green and then deep indigo-blue, changing to a reddish-violet solution on dilution, which gradually deposits brownish-red or green flocks. The corresponding *picrate* forms long, yellow needles, m. p. 202°, the *mercurichloride* long, white needles, m. p. 226° (decomp.), the *aurichloride* yellow leaflets, m. p. 200° (decomp.), the *platinichloride* orange-red needles and prisms, m. p. 233° (decomp.), and the *iodide* golden-yellow needles, m. p. 195° (decomp.). The iodide decomposes when heated in a vacuum into 4-nitrodimethyl-*o*-toluidine, $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NMe}_2$, m. p. 13.5—15°, b. p. 160°/16 mm.; hydrochloride, m. p. 197° (decomp.) (compare Gnehm and Blumer, A., 1899, i, 266). When the ammonium hydroxide is evaporated in a flask and then heated, trimethylamine, formaldehyde, and other gases are evolved, and at 170—180°/15—30 mm.; *m*-nitrodimethylaniline distils into the receiver.

IV. *Nitration of m-Tolyltrimethylammonium Nitrate*.—*m*-Toluidine is converted in the above manner into *m-tolyltrimethylammonium nitrate*, which forms prismatic crystals, m. p. 134°, the corresponding *picrate* having m. p. 108°. When boiled with fuming nitric acid, the salt yields 4-nitro-*m-tolyltrimethylammonium nitrate*, white tablets, m. p. 195° (decomp.), the corresponding *picrate* having m. p. 205°, the *iodide*, m. p. 165° (decomp.), and the *tri-iodide*, crystallising in violet-brown needles, m. p. 140°. The iodide decomposes at 210°/11 mm. into 6-nitrodimethyl-*m*-toluidine, which crystallises in dark yellow, flat, triclinic needles, m. p. 83°. This has been prepared also by methylating 6-nitro-*m*-toluidine (made from *m*-toluidine or *m*-cresol), and it corresponds with a nitrodimethyl-*m*-toluidine described by Wurster and Riedel (A., 1880, 109).

V. *Nitration of p-Tolyltrimethylammonium Nitrate*.—Dimethyl-*p*-toluidine is converted into *p*-tolyltrimethylammonium tribromide, golden-yellow leaflets, m. p. 113—115°, and then into the *nitrate*, white leaflets, m. p. 125°, and *picrate*, long, yellow needles, m. p. 195—197°, by the usual means. 3-Nitro-*p*-tolylammonium *nitrate* crystallises in glistening, white scales, m. p. 205—220° (decomp.), the *picrate* in long, yellow needles, m. p. 203°, the *tribromide* in long, yellow prisms, m. p. 152° (decomp.), the *iodide* in pale yellow prisms, m. p. 195° (decomp.), the *tri-iodide* in violet-brown prisms, m. p. 126°, and the *platinichloride* forms orange-yellow crystals, m. p. 207° (decomp.), and the *mercurichloride* long, white, prismatic needles, m. p. 141°. The *iodide* decomposes at 160°/12 mm. into 2-nitrodimethyl-*p*-toluidine, yellowish-red plates, m. p. 38°, the *picrate* having m. p. 147°. The base reacts with nitrous acid to form 2-nitrosodimethyl-*p*-toluidine, m. p. 57—59° (Pinnow, A., 1896, i, 161), and it may be obtained by methylating 2-nitro-*p*-toluidine or nitrating dimethyl-*p*-toluidine (Haibach, A., 1902, i, 444; D.R.-P. 69188).
J. C. W.

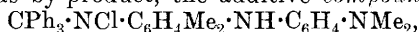
Oxidation of Secondary and Tertiary Aromatic Amines. XX. Ditertiary Hydrazines and Related Substances.

HEINRICH WIELAND (*Ber.*, 1919, 52, [B], 886—893).—Although the explanation of the mechanism of the blue colour reaction of diphenylamine advanced by Kehrman and Micewicz (A., 1912, i, 1020), and Wieland (A., 1913, i, 1386), has been generally accepted, certain details have been criticised by Marqueyrol and Muraour (A., 1914, i, 577). Thus, the removal of the imino-hydrogen atom by oxidation of the free base has been attributed by Wieland to the unsaturated nature of tervalent nitrogen; when this becomes saturated, as by salt formation, the oxidising agent appears to attack the benzene nucleus. Under similar conditions, however, the French chemists found diphenylamine to be apparently less readily oxidised in concentrated than in dilute acid solution; this is now shown to be due, however, to the consumption of the oxidising agent by side-reactions caused by the concentrated acid.

Diphenylmethylamine is readily oxidised to a carmine-red dye, which is reduced to NN'-diphenyl-NN'-dimethylbenzidine, colourless, silky needles, m. p. 171°. Diphenylmethylaminesulphonic acid is formed as a by-product of the methylation of diphenylamine with methyl sulphate; the sodium salt was analysed. The mechanism of the oxidation of salts of tertiary amines is also discussed, and it is suggested that the first stage of the process consists in the removal of the hydrogen atoms introduced with the acid, and that this is followed by oxidation of the *para*-hydrogen atoms; the first phase is then analogous to the formation of dianthrone from anthranol. The explanation is not, however, valid for triphenylamine, for which the primary addition of oxygen or hydroxyl is assumed.
H. W.

Ditertiary Hydrazines. XXI. Chlorotriarylmethanes and Diarylamines. HEINRICH WIELAND, BORIS DOLGOW, and TALBOT J. ALBERT (*Ber.*, 1919, **52**, [B], 893—898).—It has been previously shown that the dissociation products of ditertiary hydrazines unite with triphenylmethyl to yield triphenylmethyldiarylamines; attempts are now described to obtain these substances by the action of chlorotriphenylmethane on diarylamines. In general, however, derivatives of tetraphenylmethane are obtained, the formation of which is due to the transformation of the triarylmethyldiarylamines under the experimental conditions adopted: $\text{CPh}_3 \cdot \text{NPh}_2 \rightarrow \text{CPh}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{NHPh}$.

p-Anilinotetraphenylmethane, slender needles, m. p. 242° , after previous softening, is prepared by heating triphenylmethyl chloride and diphenylamine in benzene solution; it is oxidised by chromic acid in glacial acetic acid solution to a benzidine dye, and yields a *tribromo*-derivative, m. p. 214 — 215° . It can also be prepared by heating *N*-triphenylmethyldiphenylamine with diphenylamine hydrochloride in the presence of benzene, or by protracted heating of the first-named substance in glacial acetic acid solution. The action of chlorotriphenylmethane on *p*-ditolylamine, or the transformation of *N*-triphenylmethylditolylamine, leads to the formation of a *substance*, m. p. 217 — 218° , which probably has the constitution $\text{CHPh}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}(\text{C}_6\text{H}_4\text{Me})_2$. A similarly constituted compound, slender, colourless needles, m. p. 197 — 199° , is obtained from chlorotriphenylmethane and *p*-dianisylamine. Reaction between *p*-tetramethyldiaminodiphenylamine and chlorotriphenylmethane is of particular interest, since, in this instance, the primary product can be isolated, and is identical in all respects with that obtained from triphenylmethyl and the radicle $\text{N}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$ (Wieland, A., 1915, i, 848); as by-product, the additive *compound*,



is formed, which decomposes into indamine and triphenylmethane.

H. W.

The Nitro-derivatives of Phenyl- β -naphthylamine. HUGH RYAN and JAMES J. DRUMM (*Proc. Roy. Irish Acad.*, 1918, **34**, [B], (8), 165—174).—Amongst the compounds proposed for use as stabilisers for nitrocellulose powders is phenylaceto- β -naphthalide. The nature of its action has not hitherto been investigated. Since it seemed likely that the stabilising action is due to its power of combining with nitrous and nitric acids, its reaction with these substances was examined.

Nitrogen peroxide, from lead nitrate, has apparently no action on phenylaceto- β -naphthalide in dry ethereal solution. In presence of moist ether, hydrolysis and nitration occur. Phenyl- β -naphthylamine and a mononitrophenyl- β -naphthylamine, colourless, cubical crystals from xylene, m. p. 119 — 120° , are formed. The orientation of the mononitro-derivative was not determined. It was also obtained from the stabiliser and cold concentrated nitric acid.

In alcoholic solution, the stabiliser slowly forms two trinitro-compounds, m. p. 242° and 179° respectively. The same compounds are produced when a mixture of amyl nitrite, nitric acid (1—6 molecules), and the stabiliser in glacial acetic acid is allowed to remain. Under similar conditions, in the absence of amyl nitrite, no action occurs. The trinitro-compound, m. p. 179° , is also obtained when phenyl- β -naphthylamine in glacial acetic acid is treated with a large excess of nitric acid. It forms orange crystals from glacial acetic acid. The yellow trinitro-compound, m. p. 242° , is also formed when phenyl- β -naphthylnitrosamine reacts with nitric acid in glacial acetic acid, and is identical with 2':4'-dinitrophenyl-1-nitro-2-naphthylamine, which was prepared by Goldberg's method (A., 1908, i, 288) from chloro-2:4-dinitrobenzene and 1-nitro-2-naphthylamine.

The authors have also prepared the following substances by the Goldberg reaction in hot nitrobenzene:

p-Nitrophenyl- β -naphthylamine (from β -naphthylamine and *p*-bromonitrobenzene) forms yellow, matted, acicular crystals from benzene, m. p. 283 — 284° , which give a bluish-violet coloration with concentrated sulphuric acid.

Phenyl-1-nitro- β -naphthylamine (from bromobenzene and 1-nitro- β -naphthylamine) forms deep red prisms from alcohol, m. p. 105 — 106° . Its solution in cold sulphuric acid has a deep red colour.

1-Chloro-2:4-dinitrobenzene and β -naphthylamine yield a compound, red prisms, m. p. 170 — 171° . Other compounds prepared in the course of this work are: a trinitro-derivative of phenyl- β -naphthylamine, melting and decomposing at 210° , and a dinitro-derivative, brown prisms, melting and decomposing at 170 — 180° .

F. C.

Improvements in the Manufacture of Nitrophenols.

DAVID BAIRD MACDONALD and JACKSON CALVERT (Brit. Pat., 126062 and 126084).—The formation of 2:4-dinitrophenol in the nitration of benzene with nitric acid in presence of mercuric nitrate is greatly facilitated by passing carbon dioxide either into the reaction mixture or through the benzene or nitric acid contained in a separate vessel, the mixed vapours then being led into the mixture of nitric acid and mercuric nitrate in the former case, or of benzene and mercuric nitrate, together with a small portion of the nitric acid, in the latter. The reaction is allowed to proceed for about six hours at 40 — 50° , and commercially pure dinitrophenol may be isolated from the reaction mixture by simply volatilising the more volatile constituents.

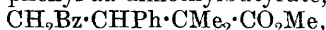
According to the second patent, air or oxygen, or a mixture of air and oxygen with or without carbon dioxide, may be substituted for the carbon dioxide there employed with similar results. [See, further, *J. Soc. Chem. Ind.*, 1919, 406A.]

G. F. M.

Pinabietic Acid, a Resin Acid from the Sulphate Cellulose Liquors. OSSIAN ASCHAN and K. E. EKHOLM (*Finska Kem. Medd.*, 1918, pp. 8; from *Chem. Zentr.*, 1919, i, 285—286).—*Pinabietic acid*, $C_{20}H_{30}O_2$, shining needles, m. p. 176—178°, has been isolated from the resin acids of the "black liquor" of the sulphate cellulose factories. When dissolved in a mixture of chloroform and acetic anhydride, the acid yields, on addition of a little concentrated sulphuric acid, a purplish-red coloration which passes through violet and blue into black. With hydrochloric acid and ferric chloride, the coloration is violet-blue. The residue obtained after evaporation with nitric acid becomes orange-yellow on addition of ammonia, instead of violet as with abietic acid. The specific rotation depends greatly on the solvent, the acid being dextrorotatory when dissolved in aromatic hydrocarbons, but lævorotatory in solution in aliphatic hydrocarbons. H. W.

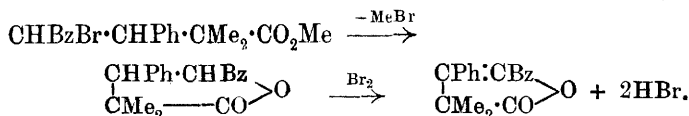
Catalytic Racemisation of Ethyl *l*-Mandelate. ALEX. MCKENZIE and HENRY WREN (*T.*, 1919, 115, 602—613).

The Bromination and Bromine Derivatives of Certain δ -Ketonic Esters. E. P. KOHLER and H. GILMAN (*J. Amer. Chem. Soc.*, 1919, 41, 683—692).—The course of the bromination of methyl γ -benzoyl- β -phenyl- $\alpha\alpha$ -dimethylbutyrate,



is found to depend on the temperature, the solvent, and the rate at which the bromine is added, the bromo-ester, saturated γ -lactones, and an unsaturated γ -lactone being formed.

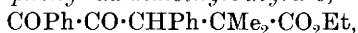
γ -Benzoyl- β -phenyl- $\alpha\alpha$ -dimethylbutyric acid is obtained by boiling together benzene, phenyl styryl ketone, and ethyl α -bromoiso-butyrate with some zinc suspended in the liquid in a copper cage, and hydrolysing the product by methyl-alcoholic-aqueous sodium hydroxide. It has m. p. 159°, and forms an *oxime*, m. p. 184.5°. The methyl ester, m. p. 92°, b. p. 200°/25 mm., is formed in the usual way from the acid (compare A., 1911, i, 863). When the ester, dissolved in chloroform, is slowly treated with bromine in the cold, the chief product is methyl γ -bromo- γ -benzoyl- β -phenyl- $\alpha\alpha$ -dimethylbutyrate, m. p. 125° (*ibid.*, 864). If the temperature is raised or the chloroform is removed by distillation instead of evaporation in a current of dry air, methyl bromide is lost, and two stereoisomeric, saturated γ -lactones are formed (*ibid.*), whilst a crotonolactone is produced if the reaction is carried out in methyl alcohol or the bromine is added rapidly, thus:



The original acid is easily converted into the δ -lactone (*ibid.*,

863), $\text{CHPh} \begin{smallmatrix} \text{CH-CPh} \\ \text{CM}_{\text{e}_2}\text{-CO} \end{smallmatrix} \text{O}$, by dissolving it in acetic anhydride containing a few drops of concentrated sulphuric acid. This lactone reacts with bromine in carbon tetrachloride to form an unstable dibromide which decomposes into the above bromo-ester and a saturated γ -lactone in methyl alcohol, but if bromination is carried out in methyl alcohol, an isomeric *bromo-ester*, m. p. 172° , is formed. The two esters both yield the γ -lactone, m. p. 115° , when left with methyl-alcoholic hydrogen bromide, but they behave differently on heating. The one with m. p. 125° decomposes at about 130° into the unbrominated ester, m. p. 92° , the corresponding acid, the γ -lactone, m. p. 115° , and the crotonolactone. The isomeride, m. p. 172° , decomposes at about 180° into benzoyl bromide, a small amount of the crotonolactone, and much uncrystallisable oil.

The above γ -benzoyl- β -phenyl- $\alpha\alpha$ -dimethylcrotonolactone is obtained in pale yellow needles, m. p. 117° , by heating the original acid with bromine in carbon tetrachloride solution. The reaction proceeds briskly at first, but the final stage requires several hours, and it obviously follows a similar course to the bromination of the ester (above). The lactone may be reduced to the original acid by means of zinc and acetic acid. It gives a deep yellow solution in alcoholic potassium hydroxide, which deposits a yellow solid on acidifying, and this soon fades and produces the lactone again. With alcoholic hydrogen chloride, the lactone forms *ethyl γ -keto- γ -benzoyl- β -phenyl- $\alpha\alpha$ -dimethylbutyrate*,



which crystallises in yellow needles, m. p. 93° , and may be hydrolysed to the free *acid*, m. p. 145° . The *dioxime* of this, m. p. 186° , is formed when the lactone is boiled with hydroxylamine hydrochloride and barium carbonate in alcohol. J. C. W.

Statics and Dynamics of the two Phthalyl Chlorides.

WILHELM CSÁNYI (*Monatsh.*, 1919, **40**, 81—92).—Phthalyl chloride exists in two tautomeric modifications, a solid and a liquid. The equilibrium in the melt is toward the side of the lower melting modification, and can only be reached from this side. The solid modification is the stable one. The equilibrium is independent of the temperature, hence the heat change accompanying the change from one modification to the other must be very small or zero. The equilibrium is set up extremely slowly at low temperatures, but with increase in temperature the velocity of the change to the stable form increases rapidly, so that at the boiling point it is almost instantaneous. The mean temperature-coefficient of the transition velocity is 1.6 for 10° . The velocity of the change was determined at 130° , the amount changed at measured intervals being deduced from the melting point of the mixture. It is shown that the reaction is unimolecular, and the velocity constant has the value 0.036. The natural melting point of the system is

practically identical with the melting point of the lower melting modification. An eutectic is formed at 8° , and consists of 23 parts of the higher melting variety to 77 parts of the lower melting variety.

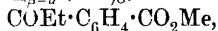
J. F. S.

Constitution of Aliphatic γ -Ketonic Acids and the Aromatic *o*-Aldehydo- and *o*-Ketonic-carboxylic Acids and their Derivatives. KARL VON AUWERS and ANNA HEINZE (*Ber.*, 1919, 52, [B], 584—601).—Some new examples of the application of optical measurements to the determination of chemical constitution.

Lævulic acid, b. p. $153^\circ/14$ mm., gives the following values: $E\Sigma_a - 0.03$, $E\Sigma_D - 0.01$, $E\Sigma_{\beta-a} + 2\%$, $E\Sigma_{\gamma-a} + 1\%$, calculated for the usual formula $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$. Its acetyl derivative, m. p. 78° , gives values which agree with the isomeric γ -lactone structure, $E\Sigma_a + 0.15$, $E\Sigma_D + 0.16$, $E\Sigma_{\beta-a} + 4\%$, $E\Sigma_{\gamma-a} \pm 0\%$, that is, it is really γ -acetoxyvalerolactone, $\text{OAc}\cdot\text{CMe} < \begin{smallmatrix} \text{CH}_2\cdot\text{CH}_2 \\ \text{O} \cdots \text{CO} \end{smallmatrix}$.

The phthalides show considerable exaltations, thus: phthalide itself, m. p. 73° , $E\Sigma_a + 0.64$, $E\Sigma_D + 0.67$, $E\Sigma_{\beta-a} + 27\%$; α -chlorophthalide, from *o*-phthalaldehydic acid and thionyl chloride, m. p. 61° , $E\Sigma_a + 0.57$, $E\Sigma_D + 0.58$; diethylphthalide, m. p. 54° , b. p. $158^\circ/17$ mm. (Bauer, A., 1904, i, 417), $E\Sigma_a + 0.51$, $E\Sigma_D + 0.56$, $E\Sigma_{\beta-a} + 25\%$. The optical properties of the ψ -esters of *o*-aldehydo- or *o*-keto-acids agree with those of the phthalides, whilst the normal esters compare with the parent aldehyde or ketones. The ψ -esters are, therefore, phthalides, as Egerer and Meyer assumed (A., 1913, i, 269). Methyl *o*-aldehydo-benzoate, m. p. 97° , has $E\Sigma_a + 0.75$, $E\Sigma_D + 0.77$, $E\Sigma_{\beta-a} + 37\%$, $E\Sigma_{\gamma-a} + 41\%$ (benzaldehyde: $+0.99$, $+1.02$, $+45\%$, $+49\%$), and the ψ -ester, α -methoxyphthalide, $\text{CO} < \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{O} \end{smallmatrix} > \text{CH}\cdot\text{OMe}$, m. p. $46\text{--}47^\circ$,

b. p. $145.5\text{--}146^\circ/12$ mm., compares with the above phthalides; $E\Sigma_a + 0.48$, $E\Sigma_D + 0.48$, $E\Sigma_{\beta-a} + 22\%$, $E\Sigma_{\gamma-a} + 22\%$. *o*-Propionylbenzoic acid, m. p. 93° , gives values which suggest that in the molten state the acid contains some of the isomeric hydroxyethylphthalide; $E\Sigma_a + 0.52$, $E\Sigma_D + 0.53$, $E\Sigma_{\beta-a} + 22\%$. The methyl ester,



from the silver salt and methyl iodide, b. p. $157\text{--}158^\circ/19$ mm., gives the values $E\Sigma_a + 0.53$, $E\Sigma_D + 0.55$, $E\Sigma_{\beta-a} + 26\%$, $E\Sigma_{\gamma-a} + 29\%$, which compare with those of propiophenone, $+0.43$, $+0.48$, $+29\%$, $+31\%$, whereas the ψ -ester, prepared by the action of the alcohol and sulphuric acid, is really α -methoxy- α -ethylphthalide, b. p. $157^\circ/17$ mm., $E\Sigma_a + 0.53$, $E\Sigma_D + 0.56$, $E\Sigma_{\beta-a} + 25\%$, $E\Sigma_{\gamma-a} + 26\%$. Methyl *o*-benzoylbenzoate, m. p. 52° , $E\Sigma_a + 0.90$, $E\Sigma_D + 0.95$, $E\Sigma_{\beta-a} + 40\%$, $E\Sigma_{\gamma-a} + 45\%$, and the ethyl ester, m. p. 58° , $E\Sigma_a + 1.00$, $E\Sigma_D + 1.06$, $E\Sigma_{\beta-a} + 39\%$, compare with benzophenone, $E\Sigma_a + 0.98$, $E\Sigma_D + 1.09$, $E\Sigma_{\beta-a} + 44\%$, whilst the ψ -ester, m. p. 56° , $E\Sigma_a + 0.52$, $E\Sigma_D + 0.57$, $E\Sigma_{\beta-a} + 23\%$, $E\Sigma_{\gamma-a} + 23\%$, is really α -ethoxy- α -phenylphthalide.

Ethyl hydrogen fumarate, m. p. 70° , $E\Sigma_a + 1.04$, $E\Sigma_D + 1.03$, $E\Sigma_{\beta-a} + 34\%$, shows greater exaltations than the normal ester, $E\Sigma_a + 0.64$, $E\Sigma_D + 0.67$, $E\Sigma_{\beta-a} + 25\%$, whereas the reverse is the case

with the phthalates; ethyl hydrogen phthalate, $E\Sigma_a + 0.42$, $E\Sigma_D + 0.41$, $E\Sigma_{\beta-a} + 22\%$, ethyl phthalate, $E\Sigma_a + 0.56$, $E\Sigma_D + 0.58$, $E\Sigma_{\beta-a} + 22\%$. Methyl phthalate, whether prepared from the silver salt and methyl iodide, from the chloride and sodium methoxide or from the anhydride, alcohol, and hydrogen chloride, has the values $E\Sigma_a + 0.56$, $E\Sigma_D + 0.57$, $E\Sigma_{\beta-a} + 24\%$, $E\Sigma_{\gamma-a} + 27\%$.

Comparing ψ -esters with the normal esters, it appears that their boiling points are very close together, but that ψ -esters have the higher densities and lower refractive indices. For the details of densities and refractive indices, the original should be consulted.

J. C. W.

The Constitution of the Truxillic Acids and of Truxone.

HANS STOBBE (*Ber.*, 1919, 52, [B], 1021—1028).—The formulæ

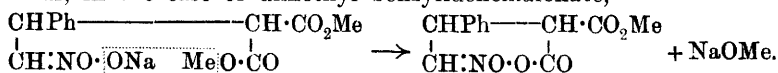
$\text{Ph}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ and $\begin{array}{c} \text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{H} \\ | \\ \text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{H} \end{array}$ have been assigned to α - and β -truxillic acids. Whilst, however, the latter may be regarded as well established, the former is not so definitely proved, and depends chiefly on the determination of the molecular weight of the amyl ester, the failure to obtain benzil by oxidation, the formation of an abnormal polymeric anhydride which does not give a fluorescein, and the conversion into truxone. The molecular weight of the latter has not been directly determined, and its formulation is deduced from its relationship to truxene, truxenequinone, and dihydrotruxone. Truxenequinone has, however, been shown to be identical with tribenzoylenebenzene, $\text{C}_{27}\text{H}_{12}\text{O}_3$, and since it is readily formed by the oxidation of truxene, it seems very probable that the latter is tribenzylenebenzene, $\text{C}_{27}\text{H}_{18}$, and that truxone has therefore the molecular formula $\text{C}_{27}\text{H}_{18}\text{O}_3$. Its formation from a number of substances, however, shows that the molecule of α -truxillic acid cannot contain more than eighteen carbon atoms, and this is supported by evidence from the molecular weights of ethyl dibromo- α -truxillate and ethyl hexachloro- α -truxillate.

To obtain further insight into the depolymerisation of the truxillic acids, the author has reinvestigated their action towards sulphuric acid; it is found that only the α -acid undergoes depolymerisation with formation of truxone, and that the latter is not directly produced from α -truxillic acid, but is formed by the action of the sulphuric acid on the *trans*- or *cis*-cinnamic acid, which is the primary product of the change. The only positive evidence in favour of the usual formula for α -truxillic acid is thereby greatly discounted, and it appears possible to the author that the α - and β -acids are structurally identical, and therefore stereoisomerides, the difference in their behaviour being due to the relative positions of the phenyl and carboxyl groups with respect to the plane of the 4-carbon ring. Support for this hypothesis is deduced from a study of the absorption curves of α - and β -truxillic acids, which are found to be even more closely similar than those of the stereoisomeric cinnamic acids.

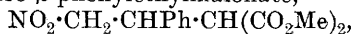
H. W.

The Addition of Nitromethane to Unsaturated Esters.

E. P. KOHLER and H. ENGELBRECHT (*J. Amer. Chem. Soc.*, 1919, **41**, 764—770).—The experiments on the interaction of alcoholic sodionitromethane and unsaturated ketones (A., 1916, i, 404) have now been extended to $\alpha\beta$ -unsaturated esters. Deep orange or red solutions are obtained which, on acidification, yield red oils which do not crystallise and cannot be purified by distillation in a vacuum. Similar results are obtained when the condensation takes place in presence of small amounts of feebly basic reagents, such as sodamide, piperidine, potassium acetate, etc. These red oils are insoluble in sodium carbonate, and their colour is not affected on acidification. They may be heterocyclic compounds formed by elimination of sodium methoxide from the metallic derivatives. Thus, in the case of dimethyl benzylidenemalonate,



It was finally shown that, in order to isolate the additive product of nitromethane and to avoid the formation of these red oils, the experiments should be made in dry methyl-alcoholic solution in presence of sodium methoxide, the mixture immediately neutralised with a little glacial acetic acid, and saturated with hydrogen chloride. Under these conditions, dimethyl benzylidenemalonate gives methyl γ -nitro- β -phenylethylmalonate,

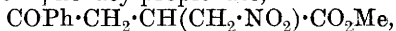


stout prisms, m. p. 63° , which is identical with the additive product of methyl sodiomalonate and β -nitrostyrene; this is an example of a new type of reaction, which is being further investigated. With alkalis, this substance is decomposed, whilst boiling hydrochloric acid yields phenylsuccinic acid. Bromine in carbon tetrachloride gives a monobromo-derivative, m. p. 158° .

The additive product of nitromethane and dimethyl cinnamylidenemalonate, $\text{CHPh} \cdot \text{CH} \cdot \text{CH}(\text{CH}_2 \cdot \text{NO}_2) \cdot \text{CH}(\text{CO}_2\text{Me})_2$, can also be obtained in benzene solution with a yield of 65%. In methyl alcohol, the yield is 87%. The nitro-ester crystallises in square plates, m. p. 74 — 75° .

The authors have prepared esters of benzoylacrylic acid by brominating esters of benzoylpropionic acid, and subsequently eliminating hydrogen bromide. *Methyl benzoylacrylate* was obtained in 92% yield as a yellow oil, b. p. 191° at 40 mm., and solidifying at 32° .

Methyl β -nitro- α -phenacylpropionate,



melts at 57° .

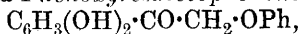
Two formulæ are possible for a substance of this type, because the ethylenic linking in the ester of benzoylacrylic acid is conjugated both with the carbonyl and with the carboxyl group. The foregoing constitution assigned to it is supported by the fact that when sodiomalonic esters combine with methyl benzoylacrylate, the sodium atom becomes attached to the carbon atom furthest from the carboxyalkyl group.

With boiling hydrochloric acid it yields benzoylpropionic acid. Bromine in chloroform gives rise to two isomeric monobromo-derivatives, separable owing to their differing solubility in cold methyl alcohol. The sparingly soluble one crystallises in plates, m. p. 125°. The other forms needles, m. p. 59°. F. C.

Bile Acids. V. MARTIN SCHENCK (*Zeitsch. physiol. Chem.*, 1919, **104**, 284—292. Compare A., 1914, i, 487).—The *isodioxime* of bilianic acid when heated with 20% hydrochloric acid yields a substance, isolated by means of its copper salt, which crystallises in white needles decomposing at 228—230°. It is believed that this product is *aminocarboxybilianic acid isooxime*, $C_{24}H_{38}O_9N_2$, formed by the opening of only one of the two lactam rings present in bilianic acid. Such an acid should contain four carboxyl groups, three of which were present in bilianic acid, but only three were titratable by direct means. It is considered that the fourth is protected by the adjacent amino-group, since an increased titration value was obtained after treatment with formaldehyde by the technique of Sörensen. Cholic acid oxime, $C_{24}H_{37}O_7N$, begins to decompose at 160°. The oxime treated with strong sulphuric acid on the water-bath gave the *isooxime*, $C_{24}H_{37}O_7N$, long, hexagonal needles, decomp. 273—275°. By the action of hydrochloric acid on the *isooxime*, a substance, $C_{24}H_{39}O_8N$, was obtained in rhombohedra, m. p. 194—195°. This is apparently *aminocarboxycholic acid*. After melting, it sets again, and finally decomposes at 274—275°, the decomposition point of the *isooxime*. These experiments support the work of Borsche and Rosenkranz (this vol., i, 276) on the structural relationship between bilianic acid and cholic acid. J. C. D.

Attempted Synthesis of Fisetol. ADOLF SONN (*Ber.*, 1919, **52**, [B], 923—928).—The synthesis of fisetol (ω -hydroxy-resacetophenone) has been attempted by several methods, which, however, have not been completely successful (compare Tambor and Du Bois, A., 1918, i, 395).

Chloroacetonitrile and resorcinol monomethyl ether react in ethereal solution under the influence of zinc chloride and dry hydrogen chloride to yield the 2-methyl and 4-methyl ether of ω -chlororesacetophenone, which are separated by taking advantage of the volatility of the latter with steam; the former has m. p. 173—174° (uncorr.). Similarly, bromoacetonitrile and resorcinol dimethyl ether yield ω -bromoacetoresorcinol dimethyl ether, m. p. 102—104° after previous softening, which is probably converted by potassium acetate into the corresponding *acetate*, prisms, m. p. 75°. Resorcinol and bromoacetonitrile yield a *product*, m. p. 127° after softening, but, as in the case of the dimethyl ether, the analytical results point to a partial displacement of bromine during the condensation. *ω -Phenoxyresacetophenone*,



forms coarse, shining plates, has m. p. 204—205° after softening at

200° (attempts to remove the phenyl group were unsuccessful); its *dimethyl ether* forms thin prisms or needles, m. p. 115° after previous softening. *ω-Ethoxyresacetophenone* has m. p. 136—137° after softening; its *diethyl ether*, coarse prisms, and *dimethyl ether*, irregular plates, have m. p.'s 66° and 56—57° respectively.

H. W.

The Preparation of β -Aminopropiophenone. WILLIAM J. HALE and EDGAR C. BRITTON (*J. Amer. Chem. Soc.*, 1919, **41**, 841—847).—Amino-derivatives of ketones cannot be satisfactorily prepared by the action of ammonia on the corresponding halogen derivatives owing to the further substitution of the hydrogen of the ammonia. Amides of ketonic acids behave abnormally in the Hofmann reaction, and give rise to internal condensation products (compare Biedermann, A., 1892, 471).

Gabriel prepared β -aminopropiophenone from *p*-bromopropyl-phthalimide. This was converted into the corresponding alcohol, acid, and acid chloride, which by the Friedel and Craft reaction and subsequent hydrolysis yielded the desired product (A., 1908, i, 181).

The author has prepared β -phthaliminopropionic acid from the *isoamyl ester* of β -chloro- or iodo-propionic acid. The yield, however, was only 40%. In order to avoid the formation of substituted phthalamic acids, the hydrolysis is effected with 40% hydrobromic acid instead of sodium hydroxide. The method finally adopted is indicated by the scheme β -iodopropionic acid \rightarrow β -iodopropionyl chloride \rightarrow β -iodopropiophenone \rightarrow β -phthaliminopropiophenone \rightarrow β -aminopropiophenone. The yields in the last stages are 90%, 68%, and 95%.

The β -chloro-derivative of propionic acid may also be used, but its preparation is less easy than that of the iodo-derivative. *isoAmyl β -chloropropionate* is miscible with most organic solvents except light petroleum, and boils at 207—208°/740 mm. The corresponding iodo-compound has b. p. 183°/140 mm. (slight decomp.). *isoAmyl β -phthaliminopropionate*, m. p. 61°, was obtained in a 70% yield from either of the two foregoing compounds.

β -Chloropropiophenone decomposes on distillation in a vacuum into hydrogen chloride and phenyl vinyl ketone.

β -Iodopropiophenone, m. p. 61° is insoluble in water and crystallises from alcohol. The acid chloride of β -iodopropionic acid is exceedingly irritating to the eyes, and readily decomposes on distillation.

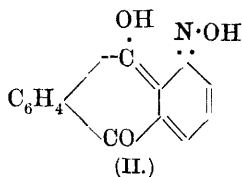
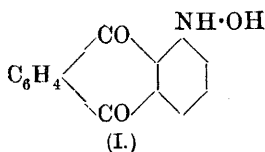
F. C.

A New Synthesis of Styryl Methyl Ketone. G. LANGLOIS (*Compt. rend.*, 1919, **168**, 1052—1054).—Acetyl chloride reacts with styrene in the presence of stannic chloride to give β -chloro- β -phenylethyl methyl ketone, which, on the addition of diethyl-aniline, loses the elements of hydrogen chloride, giving styryl methyl ketone.

W. G.

Constitution of Hydroxy- and Hydroxylamino-anthraquinone Salts. R. SCHOLL (*Ber.*, 1919, **52**, [B], 565—567).—In part, a denial of Baudisch's claim to priority (this vol., i, 211).

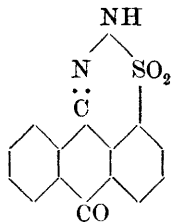
When a solution of 1-hydroxylaminoanthraquinone in alcohol is mixed with about two equivalents of sodium ethoxide and left in an atmosphere of nitrogen, a green *mono-sodium* salt is deposited. This shows that the compound behaves as a benzenoid structure (I) rather than in the isomeric form (II), which would give a disodium salt.



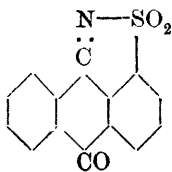
J. C. W.

Cyclic Compounds from Anthraquinone-1-sulphonic Acid.

FRITZ ULLMANN and PAUL KERTÉSZ (*Ber.*, 1919, **52**, [B], 545—558).—Anthraquinone is sulphonated in the presence of mercury, and the potassium anthraquinone-1-sulphonate (Iljinsky, A., 1904, i, 176; Schmidt, *ibid.*, 256) is heated with a mixture of phosphorus pentachloride and oxychloride at 120°. *Anthraquinone-1-sulphonyl chloride* (compare MacHoul, *Diss.*, Freiburg, 1880) crystallises from nitrobenzene or toluene in golden-yellow prisms, m. p. 218° (corr.), changes into 1-chloroanthraquinone when kept at 220°, and is hydrolysed by boiling water to *anthraquinone-1-sulphonic acid*. This forms colourless leaflets, m. p. 214° (corr.), and yields a *barium* salt, insoluble, white needles, a *calcium* salt, soluble in boiling water, a golden-yellow *lead* salt, crystallising from boiling water, a *hydrazine* salt, $N_2H_4(C_{14}H_8O_5S)_2$, and an *aniline* salt, pale yellow needles, m. p. 291°. (The *aniline* salt of anthraquinone-2-sulphonic acid is silvery-white and has m. p. 314°.)



The reactions of the sulphonyl chloride with various bases are described. Hydrazine hydrate reacts at 30° to give the *anhydride* of *anthraquinone-1-sulphonhydrazide* (annexed formula), which crystallises from aniline or nitrobenzene as a yellow powder, and yields a *sodium* salt, yellow leaflets, a *silver* salt, pale yellow leaflets, a *methyl* derivative (with methyl sulphate), silvery leaflets, decomp. 239°, and an *acetyl* derivative, pale yellow needles, m. p. 237° (decomp.).



Ammonia gives the *anhydride* of 1-anthraquinone-sulphonamide (annexed formula), which crystallises from pyridine or nitrobenzene in pale yellow, felted needles, m. p. 321° (corr.). Aniline gives *anthraquinone-1-sulphonanilide*, golden-yellow needles from toluene, m. p. 216° (corr.), and methylaniline yields *anthraquinone-1-sulphonmethylanilide*, $C_6H_4 \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} C_6H_3 \cdot SO_2 \cdot NMePh$, pale yellow leaflets, m. p. 205°.

On nitration, the potassium salt of anthraquinone-1-sulphonic acid gives a mixture of 5- and 8-nitroanthraquinone-1-sulphonic acids. The former separates directly from the hot nitrating mixture, whilst the latter crystallises slowly when the filtrate is kept (compare Schmidt, *loc. cit.*). 5-Nitroanthraquinone-1-sulphonic acid forms a golden-yellow *potassium* salt, a white *barium* salt, and a *sulphonyl chloride*, yellow needles, m. p. 277° (corr.), which reacts with ammonia to give the *anhydride* of 5-nitroanthraquinone-1-sulphonamide, this crystallising from nitrobenzene in pale brown needles, m. p. 425°, and yielding the corresponding 5-amino-compound, dark violet leaflets, on reduction with alkaline hyposulphite. 8-Nitroanthraquinone-1-sulphonic acid forms a *potassium* salt, twice as soluble as the isomeride, and a *sulphonyl chloride*, yellow needles, m. p. 245°, which yields the *anhydride* of 8-nitroanthraquinone-1-sulphonamide, m. p. 314° (corr.). The nitro-compounds may be reduced by means of potassium sulphide; *potassium* 5- and 8-aminoanthraquinone-1-sulphonates crystallise in violet needles, the 8-isomeride being the more soluble. The constitution and purity of the nitrated acids were elucidated by boiling them with hydrochloric acid and sodium chlorate, whereby they yielded 1-chloro-5-nitroanthraquinone, yellow, felted needles, m. p. 314° (corr.) (convertible into the known 1-nitro-5-aminoanthraquinone), and 1-chloro-8-nitroanthraquinone, m. p. 263° (corr.).

J. C. W.

Reduction Products of Hydroxymethylenecamphor. II. Mechanism of the Hydrogenation of Hydroxymethylenecamphor with Hydrogen and Nickel. HANS RUPE and ARTHUR AKERMANN (*Helv. Chim. Acta*, 1919, 2, 205—221. Compare this vol., i, 29).—The hydrogenation of hydroxymethylenecamphor in the presence of a specially prepared nickel catalyst can be made use of in a study of the kinetics of such reactions, and a series of experiments with this aim are now described. A graphic representation of the hydrogen absorbed from time to time shows that the curves are nearly hyperbolic when the abscissæ, x , are taken from the values, $\text{time} \times \text{weight of catalyst}/\text{initial weight of hydroxymethylenecamphor}$, and the ordinates, y , are the percentages of hydrogen absorbed, calculated on the theoretical requirement. These curves are treated mathematically, and, after making corrections for probable disturbing factors, such as secondary reactions caused by nickel compounds, it appears that the main reaction is a bimolecular one. That is, not only does the quantity of hydroxymethylenecamphor fall off, but the amount of hydrogen transferred as well, or, in other words, the catalyst continually decreases in activity. This explains why such a large quantity of nickel is required in this case to achieve a rapid and complete reduction.

In this reduction, as in so many similar cases, much more hydrogen is absorbed than is theoretically required, but, as a matter of fact, the reduction is actually complete when only about 80—90% of the required volume of gas has disappeared. This is

not due to experimental errors, but chiefly to the activation of the water by the nickel. J. C. W.

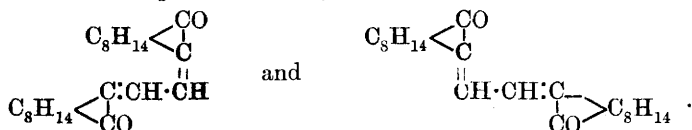
Reduction Products of Hydroxymethylenecamphor. III. New Reactions of Methylenecamphor. HANS RUPE and ARTHUR AKERMANN (*Helv. Chim. Acta*, 1919, 2, 221—233. Compare this vol., i, 29).—When camphylcarbinol is warmed with sodium in benzene solution, a new derivative, *s-dicamphylethane*,

$C_8H_{14} \begin{smallmatrix} CO \\ \diagup \quad \diagdown \\ CH \cdot C_2H_4 \cdot CH \\ \diagdown \quad \diagup \\ CO \end{smallmatrix} C_8H_{14}$, is produced. This crystallises in slender, white prisms, m. p. 209—211°, and its constitution is revealed by the fact that it may be obtained from camphylmethyl bromide by the Fittig and Wurtz method. It is assumed that water is eliminated from the carbinol, giving methylenecamphor and hydrogen (from the sodium), and that either two molecules of this compound condense and then combine with hydrogen, or one molecule is reduced to methylcamphor, which condenses with the methylenecamphor. The compound can also be obtained by boiling solutions of methylenecamphor in benzene or toluene with sodium, and then treating the product with water. In this case, the necessary hydrogen is supposed to be derived from an enolic form of the compound obtained by the union of two molecules of methylenecamphor. The fact that both series of reactions proceed better in moist benzene supports the given interpretations of the mechanism.

In the Fittig-Wurtz reactions, and in the above processes when moisture is excluded, small quantities of an *isomeride* are formed, which is slightly less soluble in light petroleum and crystallises in glistening, crossed prisms, m. p. 258—259°. Probably it has the

formula, $C_8H_{14} \begin{smallmatrix} CO \\ \diagup \quad \diagdown \\ CM_6 \cdot CH_2 \cdot CH \\ \diagdown \quad \diagup \\ CO \end{smallmatrix} C_8H_{14}$.

Chloromethylenecamphor (A., 1916, i, 409) also reacts readily with sodium in ethereal solution, giving the *cis*- and *trans*-modifications of *dicamphoethandiene*,



The *cis*-modification crystallises from light petroleum in orange-yellow tetrahedra, m. p. 238—239.5°, whereas the *trans*-isomeride is insoluble and separates best from glacial acetic acid in slender, greenish-yellow needles, m. p. 282—283°.

Camphylmethyl bromide does not react at all readily with magnesium, and its reaction with magnesium phenyl bromide is also not so vigorous as in the case of chloromethylenecamphor. The product, benzylcamphor, was also obtained with about the same optical properties by the reduction of benzylidenecamphor with sodium amalgam. J. C. W.

Studies on the Dependence of Optical Rotatory Power on Chemical Constitution. I. Position Isomerism and Optical Activity of Naphthyliminocamphors and Derivatives of Phenyliminocamphor. BAWA KARTAR SINGH and JATINDRA KUMAR MAZUMDAR (*T.*, 1919, **115**, 566—576).

Genetic Relationships of the Terpenes. OSSIAN ASCHAN (*Finska Kem. Jubiläumsnummer*, 1918, pp. 15; from *Chem. Zentr.*, 1919, i, 285).—A concise résumé of the chemistry of the terpenes.
H. W.

New Terpene in Finnish Turpentine. OSSIAN ASCHAN (*Technikern*, 1918, pp. 3; from *Chem. Zentr.*, 1919, i, 284).—A new terpene hydrocarbon has been obtained by the fractional distillation of Finnish turpentine with steam; it has b. p. 163—165°, D_4^{20} 0.8628, $[\alpha]_D + 7.70^\circ$, and is a bicyclic, simply saturated terpene closely related to pinene. It yields pinene nitrosochloride with amyl nitrite and hydrochloric acid.
H. W.

Action of Finely Divided Metals on Pinene Vapour. PAUL SABATIER, ALPH. MAILHE, and G. GAUDION (*Compt. rend.*, 1919, **168**, 926—930).—The metals used were copper, nickel, cobalt, and iron. When pinene vapour is passed over any of these metals at 350°, there is no evolution of gas, but a liquid is obtained which is less volatile than the original pinene and consists of terpenes isomeric with pinene and a small amount of polyterpenes. At higher temperatures there is an evolution of gas, the amount of which varies with the temperature and the nature of the metallic catalyst. With copper at 500° there is an abundant evolution of a gas, which is a mixture of hydrogen and olefines. With copper at 600—630° there is a still more marked evolution of gas, whilst the liquid product consists of a mixture of isoprene, olefines and diolefines, terpenes, and aromatic hydrocarbons, such as toluene, *m*-xylene, cymene, cumene, and methylethylbenzene. The yield of aromatic hydrocarbons was in one case 31% of the pinene used. With reduced nickel at 600°, a very energetic decomposition of the pinene occurs, a gas being evolved rich in hydrogen, carbon is deposited, and very little liquid product is obtained. With cobalt at 600°, the results obtained are intermediate between those obtained with nickel and copper, whilst reduced iron is similar to nickel in its effect.
W. G.

Finnish Turpentine. V. Formation of Terpin Hydrate and Terpeneol. OSSIAN ASCHAN (*Bidrag känn. Finlands natur och folk*, 1918, **77**, pp. 30; from *Chem. Zentr.*, 1919, i, 284).—The author has endeavoured to find new methods of preparing terpin from pinene and dipentene. Preliminary experiments on the action of sulphuric acid of varying concentration on oil of turpentine without cooling showed that terpin (which is probably transiently formed under all conditions when pinene is converted

into dipentene by acids) was certainly produced at the ordinary temperature, but that at the high concentration, and possibly increased temperature, water was almost immediately eliminated and dipentene formed. It is important that stirring and cooling should be very efficient, thereby preventing decomposition of the terpin hydrate formed by the acid. With efficient stirring (ten hours) and using 45% sulphuric acid, 53.2% of the theoretical yield of terpin was obtained; during the greater part of the time, the temperature must be maintained at $+1^{\circ}$. *trans*-Terpin is formed as a by-product. Terpin is also produced by the action of sulphuric acid (45%) on nopinene (from American oil of turpentine).

Terpin may also be obtained by addition of water to dipentene (1 part) by treatment with sulphuric acid (55%; 6 parts) at -6° ; the crude product is remarkably pure, but may contain *trans*-terpin. The conversion of terpin hydrate by loss of water into terpineol is best effected by the action of oxalic acid solution (0.5%). The transformation of terpineol into pinene by means of formic acid is so successful that the process appears capable of technical application. An almost quantitative yield of terpin hydrate is obtained from terpineol (1 part) by the action of sulphuric acid (40%; 5 parts), the mixture being kept well stirred and cooled by ice.

Terpin hydrate can be prepared in good yield from the fraction of Finnish turpentine, b. p. $155-167^{\circ}$, which contains the terpenes related to pinene. H. W.

Finnish Turpentine. VI. The Components of High Boiling Point. OSSIAN ASCHAN (*Bidrag k  nn. Finlands natur och folk*, 1918, 77, pp. 88; from *Chem. Zentr.*, 1919, i, 284-285).—A specimen of turpentine and a resin distillate obtained in the manipulation of the resin of *Pinus sylvestris* have been investigated, and terpene alcohol and cadinene have been obtained. The question whether cadinene exists as such in the fraction, b. p. $125-130^{\circ}/9$ mm., or whether its hydrochloride is formed by the action of hydrogen chloride on another sesquiterpene, remains undecided. H. W.

Constituents of Higher Boiling Point in Finnish Turpentine. OSSIAN ASCHAN (*Finska Kem. Medd.*, 1918, pp. 3; from *Chem. Zentr.*, 1919, i, 285).—Fractions b. p. $210-220^{\circ}$ and ca. 260° have been observed in Finnish turpentine in the products of the tar ovens and in those obtained by the distillation of resin with steam; they appear to consist of terpene alcohol and a sesquiterpene, and resemble that obtained from pine resin (preceding abstract). An unsaturated terpene alcohol, $C_{10}H_{17}\cdot OH$, has been isolated which is not identical with terpineol, but is possibly a mixture of the latter with other terpene alcohols. A sesquiterpene, $C_{15}H_{24}$, b. p. $260-263^{\circ}/760$ mm., D_4^{20} 0.9187, has also been obtained. It is unsaturated towards potassium permanganate, bromine, and hydrogen chloride, and is converted by the latter into cadinene dihydrochloride, m. p. $117-118^{\circ}$. Since cadinene, obtained from

this hydrochloride, has b. p. 271° , it cannot be identical with the original substance.

H. W.

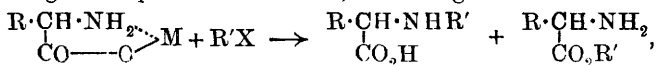
The Sesquiterpene Fraction in the Volatile Portions of Pine Resin. OSSIAN ASCHAN (*Finska Kem. Medd.*, 1918, pp. 2; from *Chem. Zentr.*, 1919, i, 285).—A new terpene has been isolated from a distillate obtained during the manipulation of pine resin. Its *dihydrochloride*, $C_{15}H_{26}Cl_2$, forms shining, rhombic leaflets, m. p. $85-86^{\circ}$. It is possibly a bicyclic sesquiterpene, and may be related to cadinene.

H. W.

Some Constituents of French and American Rosins. EDMUND KNECHT and EVA HIBBERT (*J. Soc. Dyers*, 1919, **35**, 148—154).—By repeated crystallisation from glacial acetic acid and alcohol, two pimaric acids, $C_{20}H_{30}O_2$, are isolated from French and American rosins, that from the former forming large, colourless crystals, m. p. 161° , $\alpha_D -80^{\circ}$, and that from the latter melting at the same temperature and having $\alpha_D +79^{\circ}$. The two acids differ in certain particulars, and are probably not optical isomerides. On heating in a vacuum or in a stream of carbon dioxide, both acids are converted into rosin-like anhydrides by the loss of a molecule of water from two of acid. The hydration of the anhydride of *l*-pimaric acid takes place slowly at the ordinary temperature by the action of water, and when it is crystallised from water-absorbing solvents, such as alcohol or acetic acid, inactive pimaric acid is obtained which, by ebullioscopic methods, gives figures indicating a double molecular weight. Resolution of the acid is effected by means of *d*-tetrahydroquinoline. By the action of bromine in carbon tetrachloride solution, both *d*- and *l*-pimaric acids give crystalline tribromo-substitution products, m. p. $115-118^{\circ}$, whilst with nitrous acid, greenish-blue, crystalline nitrosites, m. p. 99° , are obtained. When exposed to the air, *l*-pimaric acid slowly absorbs oxygen to the extent of two atomic proportions, and on distillation with aluminium, a hydrocarbon, $C_{19}H_{30}$, is produced, probably identical with or analogous to abietene or colophene. The rosins themselves probably consist mainly of anhydrides, hydration being a preliminary to the crystallisation of the rosin acids.

G. F. M.

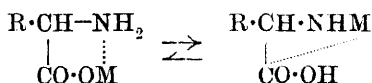
Synthetic Glucosides. III. A Contribution to the Constitution of Internally Complex Salts. P. KARRER, C. NÄGELI, and H. WEIDMANN (*Helv. Chim. Acta*, 1919, **2**, 242—265. Compare A., 1916, i, 832; 1917, i, 539).—I. *Constitution of Internally Complex Salts* [with L. WILBUSCHEWICH].—It is now generally accepted that the metallic atom in internally complex salts of the α -amino- or α -hydroxy-acids is bound, not only to the carboxyl group, but to the α -substituent as well. That being so, it should be possible to obtain isomeric derivatives by the action of a suitable halogen compound on the salt, according to the scheme:



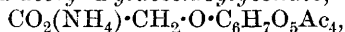
in which $\cdot\text{OH}$ might be written instead of $\cdot\text{NH}_2$. An indication that such a reaction might take place has already been given, namely, in the formation of tetra-acetylglucose salicylate and the tetra-acetylglucoside of salicylic acid by the action of acetobromoglucose on silver salicylate, and it is now shown that silver anthranilate reacts with ethyl iodide in warm toluene to form a mixture of *N*-ethylanthranilic acid and ethyl anthranilate.

In order to obtain pairs of isomerides at all, search must be made for a suitable halogen derivative. For example, silver salicylate and ethyl iodide only give ethyl salicylate. It is somewhat remarkable that acetobromoglucose is more suitable than any other derivative tested so far. This is of interest, because it opposes another interpretation of the reaction, which, without reference to internally complex salts, would suggest that any change at the α -amino- or α -hydroxyl group might be preceded by attachment of the haloid as such. Acetobromoglucose has practically no tendency to form quaternary salts with amines.

It is generally assumed that the metal is attached to the carboxylic residue by a main valency and to the amino- or hydroxyl group by residual affinity. The preponderance of ester in most of the above reactions is in keeping with this view, but it is possible to represent the salts as desmotropes, thus:



II. *Glucosides of α -Hydroxycarboxylic Acids*.—The silver salts of all the α -hydroxy-acids investigated so far react with acetobromoglucose to give isomerides, as in the case of salicylic acid. Ammonium β -tetra-acetyl-d-glucosidoglycollate,



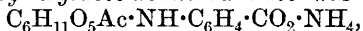
from silver glycollate, crystallises in concentric groups of felted needles, with about 2 mols. EtOH, which it loses at 95–100°, and has m. p. 157°, $[\alpha]_D^{25} - 35.6^\circ$. It yields β -d-glucosidoglycollic acid on hydrolysis with baryta or ammonia (Fischer and Helferich, A., 1911, i, 675).

Silver lactate gives *tetra-acetyl-d-glucose dl-lactate*, felted needles, m. p. 174°, $[\alpha]_D^{16} - 3.23^\circ$, and *ammonium β -tetra-acetyl-d-glucosido-dl-lactate*, m. p. 165°, $[\alpha]_D^{16} - 34.92^\circ$, which yields *d-glucosido-dl-lactic acid*, $[\alpha]_D^{17} - 36.58^\circ$, on hydrolysis.

The active and inactive mandelic acids give the following compounds: β -tetra-acetyl-d-glucosido-dl-mandelic acid, felted, white needles, m. p. 130–150°, $[\alpha]_D^{15}$ from -36.97° to -43.46° with different preparations, the corresponding derivative of *d*-mandelic acid, $\text{C}_6\text{H}_7\text{O}_5\text{Ac}_4\cdot\text{O}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$, highly refractive needles, m. p. 166°, $[\alpha]_D^{14} - 5^\circ$, and the derivative of *l*-mandelic acid, white needles, m. p. 132°, $[\alpha]_D^{15} - 82.4^\circ$; β -tetra-acetyl-d-glucose *d*-mandelate, $\text{OH}\cdot\text{CHPh}\cdot\text{CO}_2\cdot\text{C}_6\text{H}_7\text{O}_5\text{Ac}_4$, snow-white needles, m. p. 163°, $[\alpha]_D^{14} + 5.13^\circ$ (yield four times as great as that of the glucoside), and the *l*-mandelate, m. p. 134°, $[\alpha]_D^{12} - 63.09^\circ$, which is much more

soluble in alcohol than the isomeride, it being possible to separate the inactive *dl*-mandelate into the two esters by fractional crystallisation. The tetra-acetates may be hydrolysed by baryta or dilute ammonia solutions to the following: *d*-glucosido-*dl*-mandelic acid, $C_6H_{11}O_5 \cdot O \cdot CHPh \cdot CO_2H$, also designated *prulaurasinic acid*, because of its relationship to the cyanogenic glucoside, prulaurasin, a white, hygroscopic powder, crystallising with 1EtOH, $[\alpha]_D^{15} -28.17-33.18^\circ$, which is hydrolysed by emulsin, but does not reduce Fehling's solution, and forms a very hygroscopic ammonium salt, $0.5H_2O$, $[\alpha]_D^{15} -36.12^\circ$; and *d*-glucosido-*l*-mandelic acid, $[\alpha]_D^{15} -138.6^\circ$, and *d*-glucosido-*d*-mandelic acid, $[\alpha]_D^{17} +51.39^\circ$, also called *prunasinic acid* and *sambunigrinic acid* respectively.

III. *Glucosides of Anthranilic Acid*.—Silver anthranilate reacts with acetobromoglucose to form *tetra-acetylglucose anthranilate*, $NH_2 \cdot C_6H_4 \cdot CO_2 \cdot C_6H_7O_5Ac_4$, m. p. 177° , $[\alpha]_D^{15} -58.12^\circ$, and *N-tetra-acetylglucosidoanthranilic acid*, $CO_2H \cdot C_6H_4 \cdot NH \cdot C_6H_7O_5Ac_4$, white needles, m. p. 181° , $[\alpha]_D^{17} -63.89^\circ$. The latter is a representative of the somewhat obscure group of *N*-glucosides. It may be hydrolysed by methyl-alcoholic ammonia to the very hygroscopic ammonium *N-d-glucosidoanthranilate*, $[\alpha]_D^{14} -85.66^\circ$, which reduces Fehling's solution, and may be converted into the silver salt, but the free acid is too unstable to be isolated. In one hydrolysis, ammonium *N-acetyl-d-glucosidoanthranilate* was formed,

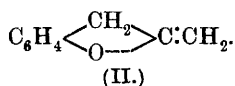
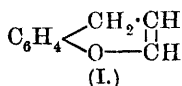


in stout, limpid crystals, m. p. $80-85^\circ$.

J. C. W.

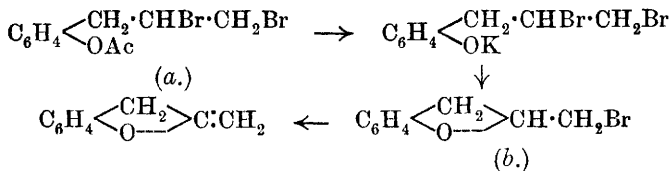
The Tannin of the Canadian Hemlock (*Tsuga Canadensis*, Carr.). RODGER JAMES MANNING and MAXIMILIAN NIERENSTEIN (T., 1919, 115, 662—673).

Cyclic Ethers from *o*-Allyl Phenols; Methylenecoumarans [1-Methylene-1:2-dihydrobenzofurans]. ROGER ADAMS and R. E. RINDFUSZ (*J. Amer. Chem. Soc.*, 1919, 41, 648—665).—The following series of reactions with *o*-allylphenol has been studied: (a) acetylation, (b) bromination, and (c) treatment of the dibromide with alcoholic potassium hydroxide. These are the reactions involved in the production of flavones by Kostanecki's method from *o*-acetoxyphenyl styryl ketones, and it was expected that in this case the parent of the flavones, namely, "chromene" (I), would be formed. Instead, the last operation takes a different course, and the product is 1-methylenecoumaran (II).



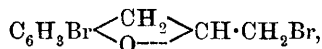
The formation of the methylenecoumaran appears to be a general reaction, and the mechanism of the process was proved as follows. When the *o*-acetoxy- β -dibromopropylbenzene is treated with one molecular proportion of sodium ethoxide, the acetyl group is eliminated and a monobromo-cyclic ether formed, which yields the known 1-methylcoumaran on reduction with zinc and hydrochloric

acid, and 1-methylenecoumaran when boiled with alcoholic potassium hydroxide. The reactions can only be interpreted as follows:



o-Acetoxyallylbenzene, from *o*-allylphenol and acetic anhydride, has b. p. 123—124°/20 mm., D^{24}_D 1.031, n^{20}_D 1.508, and its *dibromide* (a) forms white crystals, m. p. 42°; 1-bromomethylcoumaran (b) has b. p. 144—145°/20 mm., D^{25}_D 1.453, n^{20}_D 1.575; and 1-methylenecoumaran is a pleasant-smelling oil, b. p. 93—94°/20 mm., 196—197°/744 mm., D^{24}_D 1.050, n^{20}_D 1.555, which reacts with bromine in carbon disulphide at 0° to form 1-bromomethylenecoumaran, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}_2 \\ \text{O} \end{array} > \text{C} : \text{CHBr}$, b. p. 134—138°/25 mm., D^{23}_D 1.472, n^{20}_D 1.584.

In the case of *o*-allylphenol, it is necessary to acetylate before the bromination, because the free phenol reacts in a complicated manner with bromine. When slowly treated with bromine in carbon disulphide at 0° or below, and the product is slowly distilled in a partial vacuum, three main fractions are obtained. Fraction I, b. p. 90—125°/20 mm., is the greatest, and consists chiefly of 1-methylcoumaran, b. p. 93—94°/23 mm., D^{24}_D 1.032, n^{20}_D 1.531 (Claisen, A., 1913, i, 1176; 1915, i, 707). Fraction II, b. p. 125—146°/20 mm., contains two isomerides with b. p. 142°/20 mm.; one is 4-bromo-1-methylcoumaran, D^{24}_D 1.414, n^{20}_D 1.569, and the other is 1-bromomethylcoumaran, since it yields 1-methylenecoumaran when the mixture is boiled with alcoholic potassium hydroxide, and 1-methylcoumaran when boiled with zinc and hydrochloric acid. Fraction III, b. p. 180—210°/20 mm., contains chiefly α -4-dibromo-1-methylcoumaran,



b. p. 189—194°/20 mm., D^{24}_D 1.795, n^{20}_D 1.607, for, when reduced by zinc and hydrochloric acid, it yields the above 4-bromo-1-methylcoumaran, and when treated with alcoholic potassium hydroxide it forms 4-bromo-1-methylenecoumaran, b. p. 148°/30 mm., D^{24}_D 1.483, n^{20}_D 1.595.

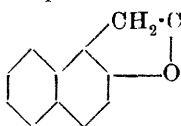
An attempt was made to obtain *o*- β - γ -dibromopropylphenol from its methyl ether. *o*-Allylanisole, b. p. 101—102°/22 mm., D^{24}_D 0.972, n^{20}_D 1.526, prepared by the action of methyl sulphate on *o*-allylphenol, reacts with bromine in carbon disulphide, however, to form some of the same compounds as the free phenol.

4-Bromo-2-allylphenol (Claisen, *loc. cit.*) yields the above 4-bromo-1-methylcoumaran when heated with pyridine hydro-

chloride, and this may also be obtained by brominating 1-methylcoumaran. 4-Bromo-2-allylphenyl benzoate has b. p. 234—236°/25 mm., D^{24}_D 1.308, n^{22}_D 1.589, and its dibromide, m. p. 98.5°, yields the above 4-bromo-1-methylenecoumaran when boiled with alcoholic potassium hydroxide.

3-Allyl-*p*-cresol and 3-allyl-*o*-cresol (*ibid.*) give the following compounds: 3-allyl-*p*-tolyl acetate, b. p. 139°/22 mm., D^{20}_D 1.022, n^{20}_D 1.507, its dibromide, long, white needles, m. p. 77.5°, and 4-methyl-1-methylenecoumaran, b. p. 113°/17 mm., D^{20}_D 1.043, n^{20}_D 1.556; and 3-allyl-*o*-tolyl acetate, b. p. 128°/14 mm., D^{20}_D 1.023, n^{20}_D 1.507, its dibromide, b. p. 210°/20 mm., and 6-methyl-1-methylenecoumaran, b. p. 101—102°/15 mm., D^{20}_D 1.043, n^{20}_D 1.553.

1-Allyl- β -naphthol (Claisen, A., 1912, i, 965) forms an acetate, b. p. 186—189°/17 mm., D^{25}_D 1.111, n^{23}_D 1.584, the dibromide of which, fibres, m. p. 89°, yields 2-methylene-2 : 3-dihydro-4 : 5- $\alpha\beta$ -naphthafuran (annexed formula), m. p. 55°, b. p. 188—190°/17 mm., when boiled with sodium ethoxide solution.



3-Allylsalicylic acid and its methyl ester (Claisen, *loc. cit.*) cannot be acetylated, but this is no hindrance to the above reaction, as the hydroxyl group needs no protection during bromination. Methyl 3- β -dibromopropylsalicylate, m. p. 72—72.5°, and the free acid, $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{CH}_2 \cdot \text{CHBr} \cdot \text{CH}_2\text{Br}$, needles, m. p. 162.5—163.5°, both yield 1-methylenecoumaran-6-carboxylic acid, m. p. 152°, when boiled with alcoholic potassium hydroxide, and this compound gives 1-bromomethylenecoumaran-6-carboxylic acid, $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_3 \cdot \text{C}(\text{CH}_2) \text{CHBr}$, m. p. 222—223°, when treated with bromine in carbon disulphide at 0°.

J. C. W.

Syntheses of Chromans and Coumarans. R. E. RINDFUSZ (*J. Amer. Chem. Soc.*, 1919, 41, 665—670).—Three simple methods for the preparation of chroman and coumaran have been discovered. I. Phenyl γ -hydroxypropyl ether, from trimethylenechlorohydrin and sodium phenoxide, is heated with zinc chloride, giving chroman in 30—35% yield, or phenyl β -hydroxyethyl ether, from ethylene chlorohydrin and sodium phenoxide, is similarly treated, giving a 25% yield of coumaran. II. Phenyl γ -bromopropyl ether or phenyl β -bromoethyl ether, from sodium phenoxide and the dibromides, heated with zinc chloride, gives a 65% yield of chroman or a 30—40% yield of coumaran as the case may be. III. Mixtures of phenol and the chlorohydrins are heated with zinc chloride, but the yields are not so good.

It is obvious that substituted chromans and coumarans could be made very readily from substituted phenols.

J. C. W.

Cinchona Alkaloids. II. 5-Azo- and 5-Amino-compounds of Cupreine, Hydrocupreine, and their Methyl and Ethyl Ethers. G. GIEMSA and J. HALBERKANN (*Ber.*, 1919, 52, [B], 906—923. Compare this vol., i, 33).—5-Benzeneazocupreine, anhy-

drous, microscopic needles, m. p. 129—130°, is obtained by the action of diazotised aniline on an alkaline solution of cupreine; the corresponding *sodium p-sulphonate* (from diazotised sulphanilic acid) forms ruby-red crystals (+6H₂O), which have m. p. 212° (decomp.) after darkening at 200°, whilst the free *p-sulphonic acid* separates from water in red, prismatic needles (+3H₂O), which, when dehydrated, decompose at 257° after darkening at 250°. Reduction of the azo-compounds, preferably with sodium hyposulphite in alkaline solution, leads to the formation of *5-aminocupreine*, an unstable, non-crystalline mass, m. p. generally between 170° and 195°, $[\alpha]_D^{20} - 121.2^\circ$ (in ether), $[\alpha]_D^{20} - 18.4^\circ$ (in alcohol). The salts are stable; the *platinichloride*, microcrystalline needles, decomposing at about 220°; the *monosulphate*, yellow, prismatic needles, which are completely decomposed at 232°; the *disulphate*, red prisms, which darken at about 170° and decompose above 200° (this is the most stable sulphate and separates from solutions containing more than the requisite quantity of sulphuric acid); the *trioxalate*, dull red powder, m. p. 152—153° (decomp.); and the *tetrasulphate*, colourless, microscopic needles, m. p. 187° (decomp.), after previous sintering and darkening, are described. *5-Benzoylaminocupreine* forms a grey powder, m. p. about 135°, after previous contraction. $[\alpha]_D^{20} + 39.8^\circ$ (in alcohol); *5-dibenzoylaminocupreine* resembles the monobenzoyl derivative, melts indefinitely at 165°, and has $[\alpha]_D^{20} + 41.6^\circ$ (in alcohol); *tribenzoylaminocupreine* crystallises in colourless, rhombic plates, m. p. 183°, $[\alpha]_D^{20} + 131.1^\circ$ (in alcohol). The primary product of the interaction of 5-aminocupreine and phenylthiocarbimide in alcoholic solution appears to be the *thiocarbamide*, small, colourless needles or plates, m. p. 247° (decomp.), after much previous softening, which, however, readily loses hydrogen sulphide and forms the corresponding *carbanilide*, colourless, anhydrous needles or rods, m. p. 185—186° (from benzene), small, monohydrated needles, m. p. 155° after previous softening (from dilute alcohol). *Cupreine-5-thioloxazole*, microscopic needles which do not melt below 300°, is obtained as by-product of the action of phenylthiocarbimide on 5-aminocupreine or, more conveniently, by the direct action of carbon disulphide on the latter; it gives a *monosulphate*, red needles (+4H₂O), which is only stable in solution in the presence of an excess of acid.

5-Aminoquinine, m. p. 214—215°, $[\alpha]_D^{20} - 22.5^\circ$ (in alcohol), -119.3° (in ether), is obtained in small yield by the methylation of 5-aminocupreine by methyl sulphate or diazomethane. *5-Aminoethylcupreine* forms prismatic needles or plates, m. p. 213—214°, $[\alpha]_D^{20} - 21.5^\circ$ (in alcohol), -121.6° (in ether); the *platinichloride* (+1H₂O), darkening at about 195° and gradually decomposing at a higher temperature; the *monosulphate*, slender needles (+3H₂O), m. p. 183—184° (decomp.) after darkening at 173° and the *disulphate*, red powder, m. p. 143° (decomp.) after darkening at 100°, are described. Reduction of aminoethylcupreine with hydrogen in the presence of palladium readily yields the *hydro-base*, m. p. 212°.

Sodium hydrocupreine-5-azobenzene-p-sulphonate is obtained in the same manner as the corresponding cupreine compound, to which it shows the closest resemblance; the corresponding *sulphonic acid* (+ 3H₂O) is also described. *5-Aminohydrocupreine* is an unstable substance which darkens above 100°, softens about 160°, and has m. p. 197° (on account of incipient decomposition the latter value is seldom observed, the m. p. usually being 180—185°); it has $[\alpha]_D^{20} -125.9^\circ$ (in ether), -24.0° (in alcohol); it gives a *monosulphate*, yellow needles, which darken at 180° and decompose without melting above 200°, and a *disulphate*, rust-red powder which decomposes above 160°. *5-Aminohydroquinine*, yellow needles, m. p. 217—218°, is obtained in the same manner as 5-aminoquinine, which it greatly resembles and from which it can be prepared by catalytic reduction; it has $[\alpha]_D^{20} -14.1^\circ$ (in alcohol), -120.6° (in ether). *5-Aminoethylhydrocupreine* forms intensely yellow crystals, m. p. 211—212°, $[\alpha]_D^{20} -123.8^\circ$ (in ether), -13.2° (in alcohol); when treated with ethyl chloroformate it yields amorphous ethylhydrocupreine ethyl urethane, m. p. 100—110°, $\alpha_D^{20} +14.8^\circ$.
H. W.

Diazo-reaction of Morphine. LUDWIG LAUTENSCHLÄGER (*Arch. Pharm.*, 1919, 257, 13—18).—Morphine and its salts couple with diazonium compounds in alkaline solution to yield dyes, the most suitable reagent being diazobenzenesulphonic acid. For qualitative work an approximately 2% aqueous solution of the latter is added to the solution of the morphine salt which is made alkaline with sodium carbonate or hydrogen carbonate; a deep red to pale red coloration, according to the concentration of the alkaloid, is immediately developed, which becomes orange after acidification with dilute acid. The limit of sensitiveness for the sodium carbonate solution is less than 1 in 10,000. The dye has little affinity for fibres in an acid bath.

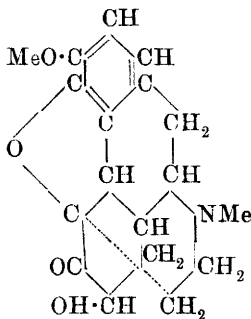
Morphine is the only member of the opium alkaloids which yields a true dye with diazonium compounds; the synthetic derivatives of morphine (dionin, heroin, peronin) do not give the reaction, whilst of the commoner pharmacological alkaloids only a few give dyes. A table is given in the original showing the colorations yielded by morphine, emetine, sparteine, physostigmine, piperidine, coniine, and nicotine with diazobenzenesulphonic acid, diazotised arsanilic acid, 2:5-dichlorobenzenediazonium chloride, *p*-nitrobenzenediazonium chloride, and benzidine tetrazotate in alkaline solution.

The constitution of the morphine dyes remains undecided, but titration with titanous chloride shows that one and two molecules of morphine are contained in the diazo- and tetrazo-dyes respectively. Methyl- and ethyl-morphine do not give the reaction. The physiological action of morphine is destroyed by its conversion into the diazonium compound. Attempts to obtain an aminomorphine by reduction of the dye under varying conditions did not lead to the desired result.

The reaction can be used for the toxicological detection of morphine in the presence of its substituents and of other alkaloids.

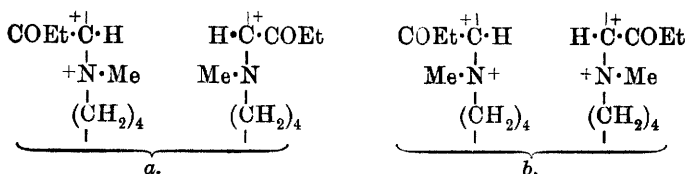
Quantitative determinations show that morphine can be estimated as accurately by the colorimetric method with diazobenzenesulphonic acid as by iodic acid or by Marquis's method; the method is most suitably applied to solutions containing 0.5—0.05 mg. of alkaloid per c.c., and has the advantage that it is not influenced by the presence of other opium alkaloids. A series of estimations of morphine in ripe poppy heads by the diazo- and iodic acid methods yielded identical results. H. W.

Oxydihydrocodeinone Hydrochloride [Eukodal]. MARTIN FREUND and EDMUND SPEYER (*Münch. med. Woch.*, 1917, **64**, 380—381; from *Chem. Zentr.*, 1919, i, 28—29).—Thebaine eliminates methyl alcohol when oxidised by hydrogen peroxide and passes into a tertiary base, $C_{15}H_{19}O_4N$, which contains only one methoxy-group and has ketonic properties; one hydrogen atom in thebaine is replaced by hydroxyl. The substance is related to codeinone, obtained by the oxidation of codeine, and, since it contains an additional atom of oxygen, is termed oxycodeinone. The aliphatic double bond in oxycodeinone is reduced by hydrogen, yielding *oxydihydrocodeinone* (annexed formula). The base crystallises in rods, m. p. 220—222°. The hydrochloride is a stable substance, freely soluble in water. The solution can be sterilised by heat without undergoing decomposition. The free base is precipitated in the crystalline form by addition of ammonia, sodium carbonate or hydroxide, and does not dissolve in an excess of alkali. Eukodal is used as a narcotic. H. W.



The Alkaloids of the Pomegranate Tree. VI. The Relationship between Methylisopelletierine, *dl*-Methylconhydrinone, and *N*-Methylpiperidylpropan- α -one. An Instance of Isomerism with Substances containing an Asymmetric Tervalent Nitrogen Atom. KURT HESS (*Ber.*, 1919, **52**, [B], 964—1004).—It has been previously shown that methylisopelletierine is α -1-methylpiperidylpropan- α -one, and that it may be formed from conhydrine (A., 1918, i, 35); a more extended examination of the latter reaction now proves that two bases are formed, one of which is identical with methylisopelletierine, whilst the other is *dl*-methylconhydrinone. Synthesis of α -1-methylpiperidylpropan- α -one leads to a product identical with the latter. The formation of methylisopelletierine from conhydrine is, however, shown not to be due to impurity in the latter, and further confirmation of the formula ascribed to it is obtained by its oxidation to α -methyl-

piperidinecarboxylic acid and acetic acid. Since the two bases yield different oximes and hydrazones, their isomerism cannot be attributed to keto-enolic desmotropy, and the author is led to the conclusion that it is due to the presence of an asymmetric carbon atom and an asymmetric trivalent nitrogen atom in the molecule. The following formulæ are then possible:



(For convenience, the piperidine ring is represented as opened at one point and placed in the plane of the paper.) Owing to the relative readiness with which methylisopelletierine reacts with semicarbazide, the formula, *a*, is tentatively proposed for it. Unexpectedly, the isomerism is still preserved when the bases are converted into their methiodides, although this phenomenon does not appear to have been observed previously with quaternary ammonium salts of the type [NABCC]X; a similar case may, however, be presented by Willstätter's dihydroarecoline methiodide and the methiodide of methyl methylhexahydronicotinate (Hess and Liebrandt, this vol., i, 220).

It has not been possible, up to the present, to cause the inter-conversion of methylisopelletierine and *dl*-methylconhydrinone.

[With FR. A. EICHEL.]—Methylconhydrine (A., 1918, i, 35) has $[\alpha]_D^{20} - 42.27^\circ$ (in water), $[\alpha]_D^{20} - 39.42^\circ$ (in alcohol). *d*-Conhydrinone (*loc. cit.*) has $[\alpha]_D^{20} - 11.42^\circ$ in aqueous solution; it gives a *hydrobromide*, m. p. 146° after previous softening, a *picrate*, m. p. $91-92^\circ$, an *ethylurethane*, b. p. $133/15$ mm., and an impure *hydrazone*, b. p. $123-125/18$ mm., which yields a *picrate*, m. p. 164° after previous softening. Methylation of *d*-conhydrinone with methyl sulphate in the presence of alkali leads to a mixture of racemic methylconhydrinone and methylisopelletierine, the ultimate separation of which is accomplished by taking advantage of the fact that the latter readily reacts with semicarbazide, to which the former is indifferent. *dl*-Methylconhydrinone is a colourless oil, b. p. $95/15$ mm.; it gives a *hydrochloride*, needles, m. p. 124° after softening from 119° , a *picrate*, cubic crystals, m. p. 106° , a *hydrobromide*, slender needles, m. p. $137-138^\circ$ after previous softening, and an oily *oxime*, b. p. $158/22$ mm., which yields a *picrate* melting to a cloudy liquid at 118° and becoming transparent at about 145° . When *d*-conhydrinone is treated with methyl iodide, the *methiodide* of the tertiary base is produced; it forms prisms, m. p. 113° , $[\alpha]_D^{20} - 2.47^\circ$.

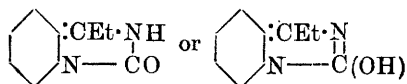
Attempts to methylate or oxidise ψ -conhydrine, under conditions which were found suitable for conhydrine, did not lead to a satisfactory result, the material being recovered unchanged.

[With H. MUNDERLOH.]— α -1-Piperidylpropan- α -ol is prepared by the catalytic reduction of α -ethylpyridyl ketone, and is obtained in two forms, m. p.'s 99—100° and 83—85° respectively, which, on methylation, yield α -1-methylpiperidylpropan- α -ols, b. p.'s 96—97°/14 mm. and 97—99°/1 mm. respectively. Oxidation of a mixture of the latter substances gives α -1-methylpiperidylpropan- α -one, b. p. 88—89°/12 mm., which is shown to be identical with *dl*-methylconhydrinone by an exhaustive examination of the picrate, hydrochloride, hydrobromide, and methiodide.

For purposes of comparison, a number of derivatives of methylisopelletierine has been prepared. The *hydrochloride* of the *dl*-base has m. p. 156° and decomposes at 160°; the *methiodide* forms cubic crystals, m. p. 156°; the *oxime* is a viscous oil, b. p. 160°/12 mm., which forms a *picrate* (or possibly mixture of picrates), m. p. 106°; the *methiodides* of the *d*- and *l*-bases also have m. p. 156°, but depression of the melting point is observed when they are mixed with the racemic form.

Methylisopelletierine is oxidised by chromic acid in sulphuric acid solution to *methylisopelletierinic acid*, which is shown to be identical with 1-methylpiperidine-2-carboxylic acid previously synthesised by Hess and Liebrandt (A., 1917, i, 354) in the form of its ethyl ester; the air-dried acid ($+\frac{1}{2}\text{H}_2\text{O}$) has m. p. 214—215° [*hydrochloride*, m. p. 205°; *platinichloride* ($+2\text{H}_2\text{O}$), m. p. 218—219° (decomp.)]; the *methiodide* of the ethyl ester crystallises in short rods, m. p. 129—131°; the *gold salt* of the methochlorides of the ethyl ester and of the acid have m. p.'s 88° and 254° (decomp.) respectively. The methiodide of ethyl 1-methylpipercolinate and some of its derivatives have previously been described by Willstätter; repetition of his work has, however, yielded products identical with those obtained from methylisopelletierine and differing in their physical constants from those described by him.

Attempts to demethylate methylisopelletierine by cyanogen bromide yielded *methylisopelletierine methobromide*, m. p. 134—136°, and the expected cyanamide derivative, b. p. 173°/14 mm.; hydrolysis of the latter gave an iminazolone derivative, probably annexed



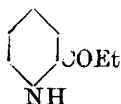
formula. The *imino-ketone*, b. p. 101—102°/14 mm., could,

however, be obtained by treatment of methylisopelletierine with ethyl azodicarboxylate; it gives a *picrate*, m. p. 154°, a *hydrobromide*, slender needles, m. p. 149°, and a *hydrochloride*, m. p. 137—138°, after previous softening.

*iso*Pelletierine is not methylated by formaldehyde and formic acid, but is converted by methyl sulphate into methylisopelletierine; *dl*-methylconhydrinone does not appear to be formed in this reaction. Attempts to convert methylisopelletierine into *dl*-methylconhydrinone by treatment with acetic and hydrochloric acids at 200°, with glacial acetic acid at 110—120°, with alcohol at 105—115°

or with alcoholic sodium ethoxide solution yielded only unchanged material and resinous or oily products. H. W.

The Alkaloids of the Pomegranate Tree. VII. Natural Occurrence of *iso*Pelletierine. KURT HESS (*Ber.*, 1919, 52, [B], 1005—1013).—During the preparation of the large quantities of alkaloids required in the investigation of methyl*iso*pelletierine (preceding abstract), the author has observed the occurrence of *isopelletierine* (annexed formula) in small amount. The alkaloids are separated in much the same manner as previously described; after removal of ψ -pelletierine by freezing, and of the bulk of pelletierine as the hydrobromide, the residual material



is distilled under diminished pressure, when considerable quantities of resin are left behind. The distillate is treated with ethyl chloroformate, and the product is repeatedly fractionated, when, after removal of α -1-methylpiperidylpropan- β -one and methyl*iso*pelletierine, a small fraction is obtained, b. p. 150—165°/13 mm., which consists of a mixture of the urethanes of pelletierine and *isopelletierine*. When hydrolysed with aqueous-alcoholic sodium hydroxide solution, the liberated pelletierine is resinified (the preparative regeneration of pelletierine from its urethane cannot be accomplished at present in spite of many variations in the conditions of the experiments), whilst the *isopelletierine* is unaffected and is obtained on distillation as an optically-inactive oil, b. p. 102—107°/11 mm. The picrate has m. p. 152° after previous softening, whereas that obtained from *isopelletierine* formed by demethylation of methyl*iso*pelletierine (preceding abstract) has m. p. 154° after previous softening; mixed m. p. 154°. The hydrobromides of the natural and synthetic bases and mixture of them melt at 149°.

The yields of the various alkaloids from 100 kilos. of the bark are approximately as follows: pelletierine, 52.5 grams; ψ -pelletierine, 179 grams; methyl*iso*pelletierine, 22 grams; *isopelletierine*, about 1.5 grams; α -1-methylpiperidylpropan- β -one, about 1 gram.

Owing to an error in calculation, the specific rotations of a number of salts of pelletierine and methyl*iso*pelletierine are incorrectly recorded in a previous paper (A., 1918, i, 404); the following are the accurate values: *d*-Pelletierine *d*-bitartrate, $[\alpha]^{20} + 21.00^\circ$, $[\alpha]^{21} + 20.93^\circ$; *l*-pelletierine *l*-bitartrate, $[\alpha]^{20} - 20.94^\circ$, $[\alpha]^{21} - 21.80^\circ$; *d*-pelletierine sulphate, $[\alpha]^{18} + 5.86^\circ$, $+ 6.11^\circ$; *l*-pelletierine sulphate, $[\alpha]^{18} - 5.89^\circ$; *d*-methyl*iso*pelletierine *d*-bitartrate, $[\alpha]^{20} + 22.77^\circ$; *l*-methyl*iso*pelletierine *l*-bitartrate, $[\alpha]^{18} - 20.83^\circ$ and $- 22.40^\circ$; *d*-methyl*iso*pelletierine sulphate, $[\alpha]^{18} + 7.64^\circ$, 8.53° ; *l*-methyl*iso*pelletierine sulphate, $- 8.03^\circ$; *d*-methyl*iso*pelletierine hydrochloride, $[\alpha]^{18} + 11.08^\circ$; *l*-methyl*iso*pelletierine hydrochloride, $[\alpha]^{18} - 10.64^\circ$. H. W.

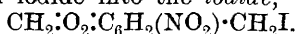
Some Derivatives of Piperonaldehyde. RUDOLF WILKENDORF (*Ber.*, 1919, 52, [B], 606—616).—I. *Quinazoline derivatives*.—

Piperonaldehyde is nitrated by dropping a concentrated acetic acid solution into well-cooled and agitated nitric acid (D 1.41), and then converted further into the oxime and reduced to *o*-aminopiperonaldoxime (Haber, A., 1891, 704). This is reduced by means of sodium amalgam and alcohol, the solution being maintained slightly acid by the addition of acetic acid, when 6-amino-3:4-methylenedioxybenzylamine is obtained as an oily base, which forms a *dihydrochloride*, bundles of long, sharp needles, decomp. 175—180°, and a yellow *mono-picrate*. When heated with sodium formate and anhydrous formic acid, the salt produces 6:7-methylenedioxy-3:4-dihydroquinazoline, $\text{CH}_2\cdot\text{O}_2\cdot\text{C}_6\text{H}_2\begin{smallmatrix} \text{CH}_2\cdot\text{NH} \\ \text{N}=\text{CH} \end{smallmatrix}$,

which crystallises in bitter needles, m. p. 153°, and forms a *hydrochloride*, bundles of needles, m. p. 267—268° (decomp.), an almost insoluble *picrate*, m. p. 234°, and an insoluble *platinichloride*, decomp. 235°. When oxidised by alkaline ferricyanide, the base yields 6:7-methylenedioxyquinazoline, m. p. 172—173° (after vacuum distillation), which gives a *picrate*, long, slender, pale yellow needles, m. p. 216°, and a *platinichloride*, decomp. 270—275°, and may be reduced by sodium amalgam to 6:7-methylenedioxy-1:2:3:4-tetrahydroquinazoline. This crystallises in glossy leaflets, m. p. 101°, and forms a *picrate*, terra-cotta-coloured tablets, m. p. 172—173° (decomp.).

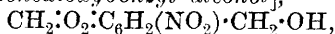
The original base forms a *triacetyl* derivative, $\text{C}_7\text{H}_7\text{N}_2\text{Ac}(\text{OAc})_2$ or $\text{C}_7\text{H}_6\text{N}_2\text{Ac}_2(\text{OAc})\cdot\text{OH}$, bundles of slender needles, m. p. 200—201°, when shaken with acetic anhydride in the cold, but the *benzoyl* derivative, $\text{CH}_2\cdot\text{O}_2\cdot\text{C}_6\text{H}_2(\text{NH}_2)\cdot\text{CH}_2\cdot\text{NHBz}$, m. p. 255°, is obtained by the Schotten-Baumann method.

II. 6-Nitropiperonyl Alcohol.—6-Nitropiperonyl chloride (Robinson and Robinson, A., 1916, i, 167) does not react at all readily with potassium carbonate solution, and was therefore converted by means of sodium iodide into the *iodide*,



This crystallises in bundles of elongated, pale yellow needles, m. p. 97—98°, but it does not irritate the skin, as the chloride does, and fails to react with silver oxide. With the idea that the iodine atom may have wandered into a ring position, the substance was chlorinated, in the expectation that a compound of the type $\text{R}\cdot\text{ICl}_2$ would be formed. During the process, however, iodine is liberated, and ultimately a *dichloro-6-nitropiperonyl chloride* is formed, either $\text{CH}_2\cdot\text{O}_2\cdot\text{C}_6\text{Cl}_2(\text{NO}_2)\cdot\text{CH}_2\text{Cl}$ or $\text{CCl}_2\cdot\text{O}_2\cdot\text{C}_6\text{H}_2(\text{NO}_2)\cdot\text{CH}_2\text{Cl}$,

pale yellow needles, m. p. 139—140°. Both the chloride and the iodide react readily with sodium acetate in alcoholic solution to form the *acetate*, tablets, m. p. 150°, which may be hydrolysed by boiling with 20% sulphuric acid to 6-nitropiperonyl alcohol [6-nitro-3:4-methylenedioxybenzyl alcohol],



this forming pale yellow crystals, m. p. 121°. The corresponding *thiocyanate*, m. p. 88—89°, is obtained by the action of potassium

thiocyanate on the chloride in boiling alcohol, and may be converted by treatment with ammonium sulphide into *di-6-nitro-piperonyl disulphide*, $[\text{CH}_2\text{:O}_2\text{:C}_6\text{H}_2(\text{NO}_2)\text{:CH}_2]_2\text{S}_2$, pale yellow needles, m. p. 103—104°. J. C. W.

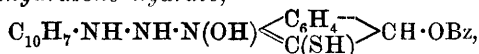
Formation and Reactions of Imino-compounds. XIX. The Chemistry of the Cyano-acetamide and Guareschi Condensations. GEORGE ARMAND ROBERT KON and JOCELYN FIELD THORPE (T., 1919, 115, 686—704).

Nitration of Diphenylethylenediamine. GEORGE MACDONALD BENNETT (T., 1919, 115, 576—578).

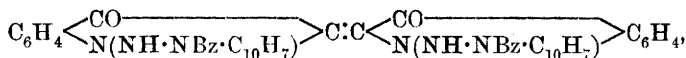
New Derivatives in the Indole and Indigotin Groups.

Isatin. III. AUGUST ALBERT and LEOPOLD HURTZIG (*Ber.*, 1919, 52, [B], 530—542. Compare A., 1915, i, 595; this vol., i, 99).—In the last paper, the behaviour of 1-oxy-2-thiol-3-benzoyloxy-3-hydroindole towards phenylhydrazine, and various reactions of the product, were described. Similar experiments with β -naphthylhydrazine are now recorded.

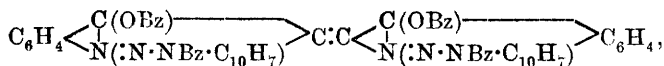
o-Nitrobenzaldehyde is converted into its cyanohydrin, from which the required material is obtained by benzoylating and then reducing with ammonium sulphide and shaking the thioamide with dilute hydrochloric acid. 2-Thiol-3-benzoyloxy-1:3-dihydroindole-1- β -naphthylhydrazone hydrate,



forms colourless needles, m. p. 120—122° (fuses to a red liquid), and reacts with 0.5*N*-sodium hydroxide to give 1:1'-*bis- β -naphthylhydrazinoindigotin*, which crystallises in dark red, lanceolate needles, m. p. 228° (decomp.), gives a brown sulphate which is easily hydrolysed, and changes into the bluish-red salt of the enolic form when covered with concentrated sodium hydroxide. The presence of two carbonyl groups is revealed by the formation of a *bisphenylhydrazone*, bundles of pale yellow needles, m. p. 183°, and the *dihydrochloride* of a *di-anil*, wine-red needles, m. p. 202°. The N:N'-*dibenzoyl* derivative,



is obtained by boiling the indigotin with 10*N*-sodium hydroxide until it is completely changed into a bluish-red powder, and then shaking with benzoyl chloride in the cold; it forms sharp, yellow needles, m. p. 184°, and gives a yellow *bisphenylhydrazone*, $\text{C}_{62}\text{H}_{46}\text{O}_2\text{N}_{10}\cdot 2\text{H}_2\text{O}$, m. p. 140—142° (after some decomposition at 107°). A *tetrabenzoyl* derivative,



is formed if an excess of benzoyl chloride is employed; it crystal-

lises in red needles, m. p. 166° , and gives the above phenylhydrazone of the dibenzoyl derivative when warmed with phenylhydrazine.

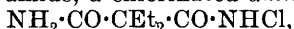
1:1'-Bis- β -naphthylhydrazinoindigotin suffers reduction by ammonium sulphide to indigotin, and by zinc dust and sodium hydroxide to 1:1'-diaminoindigotin, which is readily converted into indigotin-1:1'-imide. The acetyl derivative of this crystallises in bluish-violet needles, m. p. 212° (*loc. cit.*), and the oxime fuses and resolidifies at 290° . Reduction with zinc and acetic acid gives β -naphthylamine and the lactim form of isatin, for phenylhydrazine precipitates the α -phenylhydrazone, $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CO} \\ \text{NH} \end{smallmatrix}\rangle\text{C:N}\cdot\text{NHPh}$ (Heller, A., 1907, i, 442).

J. C. W.

Preparation of Hydantoins. CHEMISCHE FABRIK VON HEYDEN (D.R.-P. 309508; from *Chem. Zentr.*, 1919, ii, 262).—The method depends on the action of hypohalogenites on C-C-arylalkylcyanoacetamides. Thus, the sodium compound of phenylcyanoacetamide reacts with ethyl iodide to form *phenylethylcyanoacetamide*, crystals, m. p. 116° , which is dissolved by sodium hypobromite solution and yields, after short warming, *phenylethylhydantoin*, small, shining needles, m. p. $201\text{--}202^{\circ}$. Phenylallylhydantoin is similarly prepared. The arylalkylhydantoins are useful soporifics.

H. W.

Preparation of Hydantoins. CHEMISCHE FABRIK VON HEYDEN (D.R.-P. 310426, additional to D.R.-P. 309508; from *Chem. Zentr.*, 1919, ii, 262. Compare preceding abstract).—The preparation is effected by the action of hypohalogenites on malonamide. Thus, diethylmalonamide and potassium hypobromite yield diethylhydantoin. *Phenylethylmalonamide*, prepared from phenylethylcyanoacetamide and concentrated sulphuric acid at 125° , forms small leaflets, m. p. 124° (decomp.), and is converted by sodium hypobromite after some hours into phenylethylhydantoin, m. p. 201° ; if the solution is acidified immediately after solution of the amide, a chlorinated *amide*,



colourless needles, m. p. 152° , is obtained when hypochlorite is used. Diallylmalonamide yields C-C-*diallylhydantoin*, colourless needles, m. p. 204° .

H. W.

Reduction of the Nitrile Group. J. J. BLOCH (*J. Soc. Chem. Ind.*, 1919, **38**, 118—120).—The author describes a series of unsuccessful attempts to reduce the nitrile group in 5-cyanomethylbenziminazole and 5-cyanomethyl-2-methylbenziminazole (Maron, Kontorowitsch, and Bloch, A., 1914, i, 684) to the amino-group. With sodium and alcohol, reduction proceeds mainly according to the scheme: $\text{R}\cdot\text{CH}_2\cdot\text{CN} + \text{Na} + \text{H} = \text{R}\cdot\text{CH}_2 + \text{NaCN}$; with palladium hydrosol, with acetic acid and iron, sodium amalgam, aluminium amalgam, or zinc dust, only traces of base are obtained. The use of mineral acids causes hydrolysis of the nitrile. 2-Methyl-

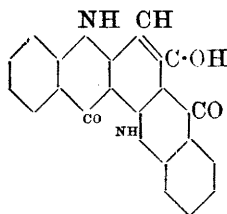
iminazolyphenylacetic acid, $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_3\langle\text{---}\text{N}\rangle\text{CMe}$, has m. p. 218—219° (anhydrous), 117° (+ 2H₂O); the mercuric salt decomposes without melting at 230°.

Reduction of benzyl cyanide with sodium and alcohol gives phenylethylamine in 35—40% yield, the process being improved by the addition of toluene. Toluene, ammonia, methylamine, and sodium cyanide are always formed, the two main reactions being the normal reduction to the amine, and $\text{CH}_2\text{Ph}\cdot\text{CN} + \text{Na} + \text{H} \rightarrow \text{PhCH}_3 + \text{NaCN}$ (compare Johnson and Guest, A., 1909, i, 784).

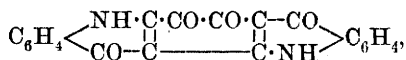
H. W.

Improvements in the Production of a Colouring Matter (*N*-Dihydro-1:2:2':1'-anthraquinone-azine). JAMES MORTON, ARTHUR GILBERT DANDRIDGE, and MORTON SUNDOWN FABRICS, LTD. (Brit. Pat., 126112).—The substitution of potassium chlorate for potassium nitrate in the preparation of *N*-dihydro-1:2:2':1'-anthraquinone-azine from 2-aminoanthraquinone by fusion at 250° with potassium hydroxide and an oxidising agent (see Brit. Pats., 3239, 22762 of 1901) results in an improved yield of dye of much greater purity, which dyes cotton to much brighter shades than can be obtained with the impure dye prepared by the older method. [See, further, *J. Soc. Chem. Ind.*, 1919, July.] G. F. M.

Structure of Hydroxyquinacridone. WL. BACZYŃSKI and ST. VON NIEMENTOWSKI (*Ber.*, 1919, 52, [B], 461—484. Compare A., 1896, i, 261).—The hydroxyquinacridone obtained by the condensation of anthranilic acid with phloroglucinol might have either a linear structure like anthracene or an angular structure like phenanthrene. Decisive evidence has been very hard to find, but the authors are now able to show that the annexed, angular, or "β" structure is correct, which is in keeping with the results of many other syntheses of quinoline derivatives with at least three nuclei.



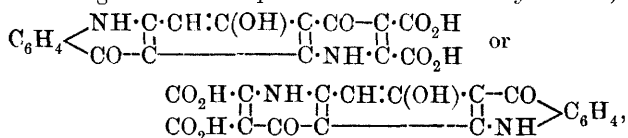
In the first place, the condensation product of phloroglucinol with *o*-aminobenzaldehyde was shown to be 4-hydroxy-β-quinacridine, because it could be oxidised to a diketone which condensed with *o*-phenylenediamine, and was therefore an *o*-diketone. Similarly, hydroxyquinacridone may be oxidised by boiling with chromic and acetic acids, or 6% nitric acid, to *diketo*-β-quinacridone,



which is a microcrystalline, red powder, m. p. 374° (decomp.), sparingly soluble in boiling quinoline or nitrobenzene, freely soluble in concentrated sulphuric acid, from which it may be precipitated again by dilution, otherwise insoluble. Unfortunately, it does

not react in the desired way with *o*-phenylenediamine, this reagent usually causing reduction to dihydroxy- β -quinacridone (see below). It does react with aniline, however, giving two *anils*, $C_{26}H_{15}O_3N_3 \cdot 3H_2O$, one soluble in ethyl acetate, forming almost black crystals, m. p. 210—230°, and an insoluble one, also black, m. p. 320°.

Oxidation with nitric acid was then tried, with the idea of obtaining recognisable degradation products, but the results were confused by the readiness with which nitration takes place. Boiling the original compound with an acid of D 1.2 gives an 80% yield of a *nitrohydroxy- β -quinacridone*, crystallising from boiling nitrobenzene in chestnut-brown needles, m. p. 330°. If the diketone is boiled with an acid of D 1.12, it gives a *nitrodiketo- β -quinacridone*, which is best obtained from the above nitrohydroxy-compound by oxidation with chromic acid; it crystallises from nitrobenzene in yellow filaments, m. p. 340° (decomp.). A *dinitrodiketo- β -quinacridone*, $C_{20}H_8O_8N_4 \cdot H_2O$, orange leaflets, m. p. 200°, is obtained if the diketo-compound is boiled with an acid of D 1.2. When the hydroxyquinacridone is boiled with 6% nitric acid (D 1.033), the main product is the diketo-derivative (above), but small quantities of a dibasic acid are formed as well. This gives the fluorescein reaction with resorcinol, and is therefore an *o*-dicarboxylic acid, formed by the destruction of one of the outside rings. *Benzo-m-phenanthrolindicarboxylic acid*, as it is called,



crystallises from acetone in pale yellow needles, m. p. 283° (decomp.), forms a *silver* salt, H_2O , a pale yellow *barium* salt, $3H_2O$, and a dark brown *compound*, decomp. 160—170°, of the formula, $\begin{array}{c} \text{CO} \cdot C_{16}H_8O_3N_2 \\ | \\ O - C[C_6H_3(OH)_2]_2 \end{array}$, when fused with resorcinol.

Better results in the oxidative degradation of the compound were obtained with permanganate. If the hydroxyquinacridone is suspended in water and gradually mixed with a saturated solution of permanganate, it is oxidised to a dibasic acid, *quinacridonic acid*, $C_6H_4 \begin{array}{c} \text{NH} \cdot \text{C} \cdot \text{CO}_2\text{H} \quad \text{CO}_2\text{H} \cdot \text{C} \cdot \text{CO} \\ \text{CO} - \text{C} \text{-----} \text{C} \cdot \text{NH} \end{array} > C_6H_4$ (or its tautomeride),

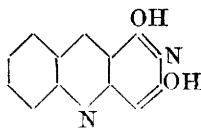
which is a white, microcrystalline powder, becoming orange at 240—255°, soft at 375°, and molten at 385°. It forms an *ammonium* salt, a *barium* salt, $3H_2O$, an *ethyl hydrogen* salt, almost white nodules, m. p. 240° (decomp.), an *ethyl ester*, canary-yellow, hexagonal tablets, m. p. 417° (corr.), and an *anhydride* (by heating at 300°), crystallising in tufts of white needles, m. p. 437° (decomp.). When heated with hydrochloric acid in a sealed tube, it yields 4:4'-*dihydroxy-3:2'-diquinolyl*, in very slender needles, m. p. 430°, which dissolves in ammonia and alkali hydr-

oxide solutions with intense blue fluorescence, and is also soluble in the more concentrated solutions of hydrochloric acid. The *potassium* salt, $6\text{H}_2\text{O}$, is obtained when a solution containing 1 part in 120 parts of boiling 20% potassium hydroxide is cooled. The chief evidence in the whole argument is the fact that this dihydroxy-compound or the quinacridone acid yields the known 3:2'-diquinolyl, $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{N}=\text{CH} & \text{CH}:\text{CH} \\ | & | \\ \text{CH}:\text{C} & \text{C}=\text{N} \end{smallmatrix}\rangle\text{C}_6\text{H}_4$, when distilled with zinc dust.

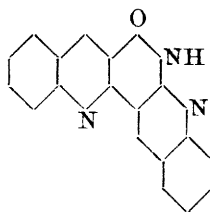
The manganese dioxide sludge obtained in the oxidation of the hydroxyquinacridone with permanganate contains unchanged material and the diketoquinacridone. The latter is easily reduced by sulphurous acid in this condition (not so when previously isolated and dried), and the *dihydroxy-β-quinacridone* so formed can be extracted with alcoholic potassium hydroxide; it crystallises in brownish-yellow granules, decomp. 425° .

Various products are obtained by the action of potassium hydroxide on 4:5-diketo-β-quinacridone. Boiling with alcoholic solutions gives quinacridonic acid; prolonged boiling with 2.5% aqueous solutions produces the pale yellow *diquinolonyleneglycollic acid*, $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{NH}\cdot\text{C}\cdot\text{C}(\text{OH})(\text{CO}_2\text{H})\cdot\text{C}\cdot\text{C} \\ | & | \\ \text{CO}-\text{C} & \text{C}\cdot\text{NH} \end{smallmatrix}\rangle\text{C}_6\text{H}_4$, which loses carbon dioxide on heating and changes into *diquinolonylenecarbinol*, orange-red needles, m. p. $456-459^\circ$ (*potassium* salt, red needles, with $2\text{H}_2\text{O}$). J. C. W.

Syntheses of 1:3-Dihydroxybenzo-2:5-naphthyridine [1:3-Dihydroxy-2:5-naphthadiazine] and a New Angular System of Five Nuclei, namely, Diquinopyridone. ST. VON NIEMENTOWSKI and ED. SUCHARDA (*Ber.*, 1919, **52**, [B], 484—492).—The condensation of *o*-aminobenzaldehyde with 2:4:6-trihydroxypyridine or glutazine differs somewhat from the reaction given by anthranilic acid (A., 1917, i, 477). Besides the expected 1:3-dihydroxy-2:5-naphthadiazine (I), there is also formed a new pentacyclic compound, "diquinopyridone" (II). The former is



(I.)

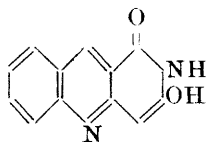


(II.)

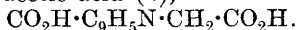
practically insoluble in glacial acetic acid, but readily soluble in alkali hydroxides, whereas conditions are reversed in the case of the second compound.

1:3-Dihydroxy-2:5-naphthadiazine (called "1:3-dihydroxybenzo-2:5-naphthyridine") crystallises in scarlet, needle-like aggre-

gates of small prisms, m. p. 375° (decomp.), and forms a yellow *hydrochloride*, $0.5\text{H}_2\text{O}$, a mono-*acetyl* derivative, glistening, golden-yellow, rectangular plates, m. p. 350° (decomp.), a mono-*benzoyl* derivative, very thin, long, golden-yellow needles, with 1AcOH , m. p. 295° (decomp.), and a *p-nitrobenzeneazo*-compound, brownish-yellow needles, m. p. 360° (decomp.). It is decomposed by heating with hydrochloric acid in a sealed tube into 2-methylquinoline and 2-methylquinoline-3-carboxylic acid, and by boiling with 25% sodium hydroxide into 3-carboxyquinolyl-2-acetic acid (?),



Diquinopyridone (II) crystallises in pale straw-yellow needles, m. p. $312\text{--}314^{\circ}$, and forms a *dihydrochloride*, but no acyl derivatives.



Because of its deep red colour and its behaviour towards acyl chlorides and hydrolytic agents, the compound may probably have a quinonoid configuration (annexed formula).

J. C. W.

Vat-like Reduction Products of the Triphenylmethane Dyes. HEINRICH WIELAND (*Ber.*, 1919, **52**, [B], 880—886. Compare this vol., i, 99).—The basic triphenylmethane dyes are readily reduced by sodium hyposulphite in aqueous-alkaline solution to colourless salts, which are re-oxidised to the dyes with extraordinary rapidity by air; the property is shared by the acid dyes such as aurin, the phthaleins, and fluorescein, which, however, are somewhat more slowly attacked by the alkaline reducing agent. The pure *sodium* salts have been isolated in the cases of crystal-violet and malachite-green, and appear to be derived from the triarylmethanesulphinic acids or the isomeric sulphonylic esters; apparently, the first stage of the reaction consists in the addition of $\cdot\text{SO}_2\text{Na}$ groups at either end of the quinonoid system, followed by the elimination of sulphur dioxide and sodium chloride. When the sulphinates are heated with an excess of alkali, the solutions lose their autoxidisability; in the case of the basic dyes, the leucobase is precipitated, whilst the solution derived from the acid dyes contains the leuco-compound. The sulphinic group is eliminated as sulphite. The course of the autoxidation has not been definitely elucidated; the main portion of the sulphonyl group is removed as sulphite, and the precipitate which is formed contains considerable quantities of carbinol, which, however, is not a primary product of the change.

H. W.

Pyrimidines. ADELHEID VON MERKATZ (*Ber.*, 1919, **52**, [B], 869—880).—2:4:6-*Trichloro-5-ethylpyrimidine*, plates or long rods, m. p. $75\text{--}77^{\circ}$, is prepared by the action of phosphoryl chloride on *sodium ethylbarbiturate* ($+2\text{H}_2\text{O}$ from aqueous solution); it is converted by concentrated alcoholic ammonia at the ordinary temperature into 2:6-*dichloro-4-amino-5-ethylpyrimidine*, needles, m. p. $214\text{--}216^{\circ}$. Fuming hydriodic acid reduces the

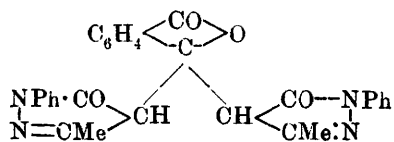
latter substance to 6-iodo-4-amino-5-ethylpyrimidine hydriodide, m. p. 204—206°. The corresponding base forms small needles, m. p. 191—193°, and yields a crystalline *hydrochloride*, *platinichloride*, and *aurichloride*; when treated with zinc dust and water, it gives the zinc double salt of 4-amino-5-ethylpyrimidine, needles, m. p. 233—235°; the free base has m. p. 163° and yields crystalline *auri-* and *platinichlorides*. The presence of the amino-group in position "4" in the pyrimidine ring follows from the non-identity of the compound with 4:6-dichloro-2-amino-5-ethylpyrimidine, which is synthesised in the following manner. Guanidine is condensed with ethyl ethylmalonate to form 2-amino-4:6-dihydroxy-5-ethylpyrimidine, which is converted by phosphoryl chloride into 4:6-dichloro-2-amino-5-ethylpyrimidine, needles, m. p. 191—192°; the latter is reduced by zinc dust to 2-amino-5-ethylpyrimidine, m. p. 142—143°, which forms double salts with mercuric, gold, and platinic chlorides. 6-Chloro-2:4-diamino-5-ethylpyrimidine is prepared by the action of alcoholic ammonia on 2:4:6-trichloro-5-ethylpyrimidine or 4:6-dichloro-2-amino-5-ethylpyrimidine; it forms plates, m. p. 183° (the *hydrochloride*, needles, the *platinichloride*, yellow octahedra, and the *picrate* are described), and is reduced by hydriodic acid and phosphorus to 2:4-diamino-5-ethylpyrimidine, m. p. 149—151°. 4:6-Diamino-5-ethylpyrimidine forms double pyramids, m. p. 233—235°; the *hydrochloride*, *nitrate*, long needles, *aurichloride*, small, yellow needles, and *platinichloride*, yellow rods, are described. 2:4:6-Triamino-5-ethylpyrimidine, m. p. 190° (corr.), is obtained from 2:4:6-trichloro-5-ethylpyrimidine and alcoholic ammonia at 210°, and is most readily purified by means of the *nitrate*; it separates from water + 1H₂O, gives a readily soluble *hydrochloride*, C₆H₁₁N₅·2HCl, a *platinichloride*, yellow needles, an *aurichloride*, minute needles, and a crystalline *picrate*.

The action of an alcoholic solution of sodium methoxide on 2:4:6-trichloro-5-ethylpyrimidine leads to the successive replacement of the three chlorine atoms by the methoxy-group, whereby (probably) 2:6-dichloro-4-methoxy-5-ethylpyrimidine, small needles, m. p. 55—57°, 6-chloro-2:4-dimethoxy-5-ethylpyrimidine, long, colourless needles, m. p. 33—34°, and 2:4:6-trimethoxy-5-ethylpyrimidine, slender needles, m. p. 67—68° (crystalline salts with gold, platinic, and mercuric chlorides), are formed. The constitution of the second of these substances follows from its reduction to 2:4-dimethoxy-5-ethylpyrimidine, b. p. 234—236° (corr.) (the *aurichloride* and *platinichloride* salts are crystalline), and demethylation of the latter to 5-ethyluracil, m. p. 300—303° (decomp.).

Attempts to prepare derivatives of 4-phenyl-6-methylpyrimidine by the condensation of benzoylacetone with carbamide did not lead to the desired result; by using thiocarbamide, however, the thiolpyrimidine was readily prepared, in which the mercapto-group was replaced by the hydroxy-group by treatment with dilute aqueous-chloroacetic acid solution in accordance with the directions of Wheeler and Liddle (A., 1908, i, 692); it is interesting to note

that the thioglycollates, assumed by these authors to be formed a intermediate products, are actually isolated in the present instance 2-Thiol-4-phenyl-6-methylpyrimidine forms amber-coloured rhombs m. p. 199—200°; 4-phenyl-6-methylpyrimidine-2-thioglycollate ha: m. p. 85°; 2-hydroxy-4-phenyl-6-methylpyrimidine crystallises in yellow needles, m. p. 228—229° (hydrochloride, long needles picrate, crystalline aggregates; platinichloride, granular; aurichloride, small needles). 2-Chloro-4-phenyl-6-methylpyrimidine has m. p. 50—51° (hydrochloride, colourless needles); it is reduced by hydriodic acid and red phosphorus to 4-phenyl-6-methylpyrimidine, m. p. 44—45° (hydriodide, yellow crystals; the aurichloride, platinichloride, and picrate are crystalline). H. W.

Condensation of 1-Phenyl-3-methylpyrazol-5-one with Anhydrides. SARAT CHANDRA CHATTERJEE and ANANDA KISHORE DAS (*J. Amer. Chem. Soc.*, 1919, **41**, 707—709).—Antipyrine condenses with phthalic anhydride



(2 mols. to 1) at 180° to form a compound of the annexed formula, which crystallises in bright red needles, m. p. 212°. Succinic anhydride at 165° gives a similar compound, m. p.

184°. Benzoic and camphoric anhydrides give no definite products.

J. C. W.

Condensation Products from Amine Salts, Formaldehyde, and Antipyrine. U. MANNICH and B. KATHER (*Arch. Pharm.*, 1919, **257**, 18—33. Compare Mannich and Krösche, A., 1913, i, 101).—Antipyrine and formaldehyde react readily with the salts of secondary and primary, but not of tertiary, amines in aqueous solution, forming salts in which the hydrogen atom attached to the 4C-atom of antipyrine is replaced by the methyl group. (For the radicle, $-\text{CH}_2 \cdot \text{C}_{11}\text{H}_{11}\text{ON}_2$, the nomenclature antipyrinomethyl- is proposed.) Direct condensation between formaldehyde and antipyrine can frequently be completely prevented or hindered by addition of a small quantity of pyrimidone to the mixture. The substances behave similarly to those obtained from ammonium chloride, and are decomposed into the constituents by sulphurous acid. The new bases are somewhat closely allied to pyrimidone, but, however, do not show any antipyretic action. Their formation appears to depend on the mobility of the hydrogen atom influenced in antipyrine by the proximity of the double bond and the carbonyl group; attempts to obtain similar derivatives from substances similarly constituted in this respect failed in the cases of 1-phenyl-3-methylpyrazol-5-one, 1-phenyl-5-methylpyrazol-3-one, dimethylaniline, and barbituric acid, but succeeded with malonic acid and its monoalkyl derivatives and with 1-phenyl-2:5-dimethylpyrazol-3-one. The following individual substances are described:

antipyrinomethyl dimethylamine, $\begin{array}{c} \text{NPh} \cdot \text{CO} \\ | \\ \text{NMe} \cdot \text{CMe} \end{array} \text{C} \cdot \text{CH}_2 \cdot \text{NMe}_2$, small

prisms, m. p. 93—94°, which do not yield the colour reactions of antipyrine, and are decomposed into other components by boiling dilute hydrochloric acid (10%) or by sulphurous acid; *hydrochloride*, fine needles, m. p. 208°. *Bisantipyrinomethylmethylamine*, $\text{NMe}(\text{CH}_2\cdot\text{C}_{11}\text{H}_{11}\text{ON}_2)_2$, needles (+ 2H₂O), m. p. 111°. *Antipyrinomethyldiethylamine*, short prisms, m. p. 68°. *Bisantipyrinomethylethylamine*, slender needles, m. p. 143°. *Bisantipyrinomethylallylamine*, shining prisms, m. p. 163° (the base unites with two atoms of bromine in chloroform solution, but the product is not crystalline). *Ethyl bisantipyrinomethylaminoacetate*, needles grouped in rosettes, m. p. 174°. *Bisantipyrinomethyl-ac-tetrahydro-β-naphthylamine*, small, shining leaflets, m. p. 217°. *Antipyrinomethylpiperidine*, plates, m. p. 99°. *Antipyrinomethyltetrahydroquinoline*, slender needles (+ 1H₂O), m. p. 153°. *Bisantipyrinomethyl-ω-aminoacetophenone*, slender needles, m. p. 93°; *hydrochloride*, small leaflets, m. p. 96°. *Tetra-antipyrinomethylethylene-diamine*, shining prisms, m. p. 179°. *Bisantipyrinomethylpiperazine*, m. p. 248° (prisms + 4.5H₂O). *Antipyrinomethylmethyl-aniline*, small prisms, m. p. 140°. *isoAntipyrinomethyldimethylamine*, $\begin{matrix} \text{NPh}\cdot\text{CMe} \\ \text{NMe}-\text{CO} \end{matrix} > \text{C}\cdot\text{CH}_2\cdot\text{NMe}_2$, small prisms (+ 1H₂O), m. p. 66°.

Condensation products could not be isolated from antipyrine, formaldehyde, and hydrazine hydrochloride or guanidine hydrochloride respectively.

H. W.

Preparation of Monoazo-dyes. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 309951; from *Chem. Zentr.*, 1919, ii, 179).—Diazotised 5-nitro-2-aminobenzamides, in which the two hydrogen atoms of the amino-group are replaced by alkyl, aryl, or aralkyl groups, are coupled with the sulphonic acids of β-naphthylamine or its derivatives in acid solution. The products dye wool in red to violet shades from an acid bath, and the dyes are fast to light and rubbing. The nitro-2-aminobenzamides are obtained by the action of secondary aliphatic or aromatic amines on nitroisatoic acid. The following individual members are described: 5-nitro-2-aminobenz-methylanilide, m. p. 183—184°; 5-nitro-2-aminobenzethylanilide, m. p. 144—145°; 5-nitro-2-aminobenzdimethylamide, m. p. 213—214°; 5-nitro-2-aminobenzpiperidide, m. p. 163—164°; 5-nitro-2-aminobenzethyl-*o*-toluidide, m. p. 147—148°. H. W.

Formation of Diazoamino-compounds from β-Naphthylamine. GEORGE MARSHALL NORMAN (T., 1919, 115, 673—679).

Extension of the Theory of Isoelectric Point. Competitive Action of other Ions with H⁺ and OH⁻ Ions in the Precipitation of Denatured Albumins. LEONOR MICHAELIS and PETER RONA (*Biochem. Zeitsch.*, 1919, 94, 225—239).—The coagulation of denatured albumins is dependent on the hydrogen-ion concentration. Salts may exert a two-fold action. First, it is shown that other ions than H⁺ and OH⁻ ions may exert an influence on the process. In general, anions displace the optimal hydrogen-ion concentration for flocculation towards the acid side, whereas cations

exert an opposite effect. The action of the ions is in accordance with the ionic series. Secondly, there may be an inhibition or strengthening of the maximal precipitation at the isoelectric point, as compared with the maximum precipitation in the absence of salts. The earths exert the strongest inhibitory influence, that of the alkalis being less, whilst the heavy metals bring about the reverse effect. Of the anions, chlorine and bromine inhibit, whereas the iodine and CNS ions do not. These actions are a result of a competitive process between other ions and the H^+ and OH^- ions for the protein, which can bind or adsorb them in different amounts. Further knowledge must be based on a systematic investigation of the adsorption of ions by simple adsorbents. J. C. D.

Lysine as a Hydrolytic Product of Hordein. CARL O. JOHNS and A. J. FINKS (*J. Biol. Chem.*, 1919, **38**, 63—66).—Analyses of hordein by the method of Van Slyke indicate that the basic amino-acids are present in the following proportions: cystine 1.18%, arginine 2.82%, histidine 2.27%, and lysine 0.89%. The free amino-nitrogen present in this protein corresponds with one half the lysine nitrogen.

These values agree with those representing the distribution of the basic amino-acids in gliadin from wheat. J. C. D.

Casein. L. A. MAYNARD (*J. physical Chem.*, 1919, **23**, 145—153).—The author has repeated and confirmed the work of Plimmer and Bayliss (A., 1906, i, 325) on the action of 1% sodium hydroxide on casein. It is also shown that the phosphorus of the casein molecule is split off and changed into a soluble inorganic form by the action of 1% sodium hydroxide at 25° for long periods of time. At the same time, the loosely combined sulphur is also split off. On the addition of acids to the sodium hydroxide digest at the end of the digestion, a white precipitate is obtained which, although not identified, has been examined with reference to its dissimilarity from casein. It exhibits colloidal properties similar to those of casein as regards its behaviour with acids and bases. It responds to the various protein tests in the same way as casein, and is similarly precipitated by salts. Its solubility in various reagents is markedly different from that of casein, and a solution in lime-water is quite different from a similar solution of casein. When phosphoric acid was introduced into a lime-water solution, in such a way as not to destroy the colloidal solution, a milky solution was obtained which, on heating, behaved in the same way as a lime-water solution of casein. This reaction furnishes evidence in support of the hypothesis that the white colour of milk is due to the peptisation of calcium phosphate by the colloids in the milk. Attempts to cause this substance to adsorb phosphoric acid were unsuccessful, but the experiments do not necessarily show that such a combination is not present in casein, for both sulphur and albumoses are also split off by sodium hydroxide, and it may be that their presence is essential for the adsorption of phosphorus.

J. F. S.

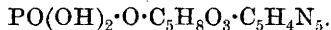
Hæmocyanin. I. Reduction of Oxyhæmocyanin by Physical and Biological Means. FILIPPO BOTTAZZI (*J. Physiol. Pathol. gén.*, 1919, **18**, 1—7).—According to Alsberg and Clark (A., 1915, i, 67), oxyhæmocyanin of *Limulus* scarcely gives up any oxygen in a vacuum. The author finds this to be the case for *Octopus* blood, unless it is exposed in thin layers to a very high vacuum, when it is slowly, but completely, decolorised by loss of oxygen. This reduction is also effected by the living leucocytes, even if they are collected as a deposit by centrifuging. If the leucocytes are killed by acids, chloroform, ether, formalin, or are completely removed after centrifuging, the blood remains blue.

G. B.

An Optically Inactive Sodium Nucleate. R. FEULGEN (*Zeitsch. physiol. Chem.*, 1919, **104**, 189—210).—The preparation of a sodium salt of thymus-nucleic acid is described which is optically inactive and will not gelatinise. On the addition of acids, the activity and power of gelatinisation return, and the changes are reversible. The acid groups which hold the sodium in the alkaline salt must be very weak, for the addition of carbon dioxide or acetic acid results in the formation of the active salt. A number of observations are recorded which indicate that the structural changes which underlie the changes in physical properties may occur without corresponding changes in the degree of dissociation of the weak acid groups. It is suggested that these groups are not free in the active molecule, but that they are bound in a form which is sensitive to alkalis, acids, or rise in temperature.

J. C. D.

Adenine Mononucleotide. WALTER JONES and R. P. KENNEDY (*Journ. Pharm. Exp. Ther.*, 1919, **13**, 45—53. Compare this vol., i, 294).—When a neutral or faintly alkaline solution of nucleic acid is oxidised with potassium permanganate, the various groups are destroyed in a definite order, and a residue is obtained from which no cytosine, uracil, or guanine can be isolated after acid hydrolysis. From this residue, an adenine mononucleotide has been isolated crystallising in needles, and giving rise to a crystalline brucine salt, m. p. 173—174°. On the grounds that the nucleotide is a dibasic acid and that it yields adenine on mild acid hydrolysis at a much more rapid rate than it does phosphoric acid, it is concluded that the structure must be



This formula is in accordance with everything that is known of the substance.

J. C. D.

The Effect of Hydrogen Ion Concentration on the Liquefaction of Gelatin. HARRISON E. PATTEN and ALFRED J. JOHNSON (*J. Biol. Chem.*, 1919, **38**, 179—190).—The setting of gelatin is influenced by the hydrogen-ion concentration of the medium, and unless the gelatin is destroyed, this effect is probably reversible.

Gelatin in the concentrations used is not without effect on the buffer solutions, displacing the p_H in such a manner as would be expected from an aggregate of amino-acids acting amphotERICALLY.

J. C. D.

New Theories of the Formation and Action of Diastase.

J. WOHLGEMUTH (*Biochem. Zeitsch.*, 1919, **94**, 213—224).—The author cannot confirm the work of Biedermann (A., 1916, i, 62), who found a diastatic action in boiled starch solution. He is also unable to confirm the experimental results of Woker (A., 1916, i, 61, 447), who claimed that formaldehyde could exert a diastatic action. The severe criticisms of the latter author's work advanced by Kaufmann (A., 1916, i, 62) are supported. A quantitative recovery of starch may be effected after treatment with formaldehyde for twenty-four hours if the aldehyde is removed by phenylhydrazine and alcohol. The starch so recovered gives the typical reactions. The action of the formaldehyde must be, as Kaufmann suggested, due to a combination with the groupings which react with iodine.

J. C. D.

Fixation of Formaldehyde by Enzymes. TH. BOKORNY (*Biochem. Zeitsch.*, 1919, **94**, 69—77).—The fixation of formaldehyde by emulsin was studied quantitatively, and from the amount found, assuming that combination of the aldehyde and free amino-groups in the emulsin occurs, it is estimated that 4% of the enzyme is represented by such groups in a reactive state. Previous experiments (A., 1915, i, 1018) gave a lower percentage, but this may be due to differences in the purity of the two preparations. The author interprets these and other results as evidence that emulsin possesses a protein nature.

J. C. D.

Biochemical Synthesis of Cellobiose by means of Emulsin.

EM. BOURQUELOT and M. BRIDEL (*Compt. rend.*, 1919, **168**, 1016—1019).—From the residue left, after extracting gentiobiose and the mono- and di-glucosides of ethylene glycol obtained in the action of emulsin on a mixture of ethylene glycol, dextrose, and aqueous alcohol (see this vol., i, 137), the authors have now isolated and characterised cellobiose.

W. G.

Oxidising Enzymes. I. The Nature of the " Peroxide " Naturally Associated with certain Direct Oxidising Systems in Plants.

MURIEL WHELDALÉ ONSLOW (*Biochem. J.*, 1919, **13**, 1—9).—If the tissues of certain plants (pear, potato, apple, and greengage) which give direct oxydase reactions are extracted with alcohol, something is removed which is part of the system responsible for the reactions. An aqueous extract of the alcohol insoluble fraction will not darken on exposure to air, nor will it give a blue coloration with guaiacum tincture until hydrogen peroxide is added. If these aqueous extracts, which contain the peroxidase, are treated with catechol or protocatechuic acid, they

darken on exposure and will give the guaiacum reaction. The pear oxydase added to a crude solution of caffeic acid, followed by guaiacum tincture, gave a blue colour. There is reason to believe that the tissues of all plants which turn brown on injury and give the direct reaction with guaiacum will behave in the same manner with catechol and subsequently towards guaiacum. Tissues of plants which normally do not give the direct oxydase reactions failed to yield extracts which oxidised catechol. It is possible that tannin may exert an inhibitory action in some cases. A substance is extracted from pears and potatoes by hot alcohol which is precipitated by lead acetate, is soluble in ether, and gives the reaction with ferric chloride and sodium carbonate characteristic of the orthodihydroxy-grouping of catechol.

The direct oxydases of plants prepared by precipitation of the expressed juices with alcohol have been termed laccases, but it appears probable that these complexes are precipitates containing the crude peroxydase and, in addition, the oxidised aromatic substance in an adsorbed condition. The conception of the oxydase system as formulated by Bach and Chodat is extended. The direct oxydase system in the pear fruit and potato tuber is due to the presence of peroxydase and an aromatic substance, giving reactions characteristic of the catechol grouping. On injury, the peroxydase activates the oxidation of the aromatic substance, with the formation of a peroxide. The peroxide-peroxydase system so formed will then give a blue coloration with guaiacum.

J. C. D.

Physiological Chemistry.

Non-protein Nitrogen of Human Blood. JOH. FEIGL (*Biochem. Zeitsch.*, 1919, **94**, 84—128).—A detailed discussion of the significance of variations in the non-protein nitrogen of the blood, with especial reference to pathological conditions.

J. C. D.

Formation of Glycogen and Sugar at the Expense of Fats. RAPHAEL DUBOIS (*Compt. rend. Soc. Biol.*, 1918, **81**, 689—691; from *Chem. Zentr.*, 1919, i, 113).—The author's experiments, since 1888, with the marmot lead him to the conclusion that sugar and glycogen can be formed directly from fats and indirectly from proteins.

H. W.

The Fat-soluble Accessory Substance. I. Its Nature and Properties. JACK CECIL DRUMMOND (*Biochem. J.*, 1919, **13**, 81—94).—The fat-soluble accessory growth-promoting factor as present in animal fats is not as stable to high temperatures as has

been assumed. The growth stimulating action of the factor present in butter and whale oil may be destroyed by exposure to a temperature of 100° for as short a time as one hour. Lower temperatures may cause destruction, but the process is not so rapid. In the case of whale oil, exposure to 37° for several weeks was found to cause a great deterioration in the amount of the accessory factor present. As far as could be ascertained, this was not due to changes of an oxidative or hydrolytic nature. The vitamine is not extracted from oils by water or dilute acids, but it may be partly removed by extraction with alcohol. Saponification of oils containing the accessory factor, even when conducted at the ordinary temperature and in the absence of water and oxygen, results in disappearance of the growth-stimulating properties. Fat-soluble *A* could not be identified with any known components of fats or with substances frequently associated with fats, such as cholesterol, phosphatides, or pigments. It is suggested that the vitamine may be an ill-defined body resembling an enzyme. J. C. D.

The Fat-soluble Accessory Factor. II. Its Rôle in Nutrition and Influence on Fat Metabolism. JACK CECIL DRUMMOND (*Biochem. J.*, 1919, **13**, 95—102).—The fat-soluble vitamine is necessary for maintenance of health in the adult, although for this purpose relatively smaller quantities are required than are necessary for growth and well-being in the young. No obvious pathological lesion has been observed to be a specific result of a deficiency of this accessory factor, but animals so deprived show a very much impaired resistance to bacterial invasion. No direct connexion between the fat-soluble *A* and fat metabolism could be traced. Absorption of fat or fatty acids from the intestinal tract is good, even when the animals are showing a decline in health as a result of the deficiency of this vitamine. J. C. D.

Rôle of the Antiscorbutic Factor in Nutrition. JACK CECIL DRUMMOND (*Biochem. J.*, 1919, **13**, 77—80).—The dietary requirements of the higher animals include, in addition to a satisfactorily balanced ration of proteins, fats, carbohydrates, and mineral salts, an adequate supply of three accessory food factors: (i) fat-soluble *A*; (ii) water-soluble *B*; (iii) the antiscorbutic factor, or water-soluble *C*. This confirms the results of Harden and Zilva (this vol., i, 186). J. C. D.

Is Lactalbumin a Complete Protein for Growth? A. D. EMMETT and G. O. LUKOS (*J. Biol. Chem.*, 1919, **38**, 147—159).—Lactalbumin is a complete protein in the sense that it is not lacking in any essential nitrogenous cleavage product necessary for growth. Under some conditions, however, diets containing lactalbumin as a sole source of protein do not permit good growth in rats (see also McCollum, A., 1919, i, 186). This is explained by assuming that lactalbumin is either sensitive to certain toxic sub-

stances or that it is a protein unable to adsorb a vitamine other than water-soluble *B*. Lactose added to such unsatisfactory diets has a good effect, which may be due either to its power of overcoming the toxic agent, or to it carrying a water-soluble vitamine other than water-soluble *B*.
J. C. D.

The Retention Power of the Kidney for Dextrose. Can the Calcium in the Perfusion Fluid be Replaced by Strontium, Barium, or Magnesium? H. J. HAMBURGER and C. L. ALONS (*Biochem. Zeitsch.*, 1919, **94**, 129—130).—The author has previously shown that dextrose may be retained by the frog's kidney perfused with a modified Ringer's solution (Hamburger and Brinkman, *Proc. K. Akad. Wetensch. Amsterdam*, September, 1917). When the perfusion fluid contains 0.06% of dextrose and the calcium is replaced by an equivalent amount of strontium or barium, the sugar is retained by the kidney, but such is not the case when an equivalent amount of magnesium is employed. If the solution is hypertonic with regard to dextrose, 0.1%, the same amount of sugar is found in the urine whether the perfusion fluid contains calcium, barium, or strontium.
J. C. D.

The Formation of Phenol. MIDORI TSUDJI (*J. Biol. Chem.*, 1919, **38**, 13—16).—Phenol, but not cresol, is formed from tyrosine by the action of *Bacillus coli communis*. Phenol was not formed from phenylalanine. The significance of these observations with regard to the formation of phenols in the animal body is considered.
J. C. D.

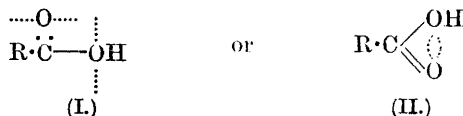
Bioluminescence. RAPHAEL DUBOIS (*Compt. rend. Soc. Biol.*, 1918, **81**, 484—485; from *Chem. Zentr.*, 1919, i, 241).—The investigations of Harvey (A., 1917, i, 365; 1918, i, 89) do not justify the replacement of the nomenclature "luciferase" by another name [compare Harvey, this vol., i, 299].
H. W.

The Relationship between Odour and Chemical Constitution. THOMAS H. DURRANS (*Perfumery and Essent. Oil Rec.*, 1919, **10**, 104—136).—The author gives a systematic survey of various classes of chemical compounds containing only carbon, hydrogen, and oxygen, or only two of these elements, and attempts to trace the cause of their odour or the lack of it, certain general conclusions being drawn for each class of compound. It is obvious that certain groups and linkings are sources of odour, but there are undoubtedly other powerful influences at work. Woker's theory that intramolecularly repelling forces increase the volatility of a compound, and consequently its odour, is partly correct, but breaks down with certain classes of ring compounds. A moderate molecular weight increases an odour, but a high molecular weight undoubtedly suppresses it. In certain circumstances, the closing of a ring does not affect the odour much, although in other not very different cases the effect is quite marked.

If the various osmophores, or sources of odour, are examined, it will be noticed that there is always a possibility of unsatisfied partial valencies or residual affinities existing, for example, the oxygen atom, the benzene ring, multiple linking, etc., all sources of odour and all possessing residual affinities. The author believes that such unsatisfied residual affinities are the prime cause of a chemical substance having an odour. If these affinities can be satisfied intramolecularly, no odour results. Thus the alcohols have unsatisfied residual affinities, the glycols have not; the alcohols have an odour, the glycols have not. It is necessary to assume that these



residual affinities can, under certain conditions, neutralise one another, and thus produce no odour, this neutralisation being influenced by the proximity of various groups. Thus with acids we may have



according as R is a light or a heavy group, substance I having an odour and substance II being odourless. On esterifying with an alcohol of low molecular weight, odour is again produced.

W. G.

Oxyhydrase, an Oxidising Reducing Ferment. Its Antitoxic Function. J. E. ABELOUS and J. ALOY (*Compt. rend. Soc. Biol.*, 1918, **81**, 783—785; from *Chem. Zentr.*, 1919, i, 383).—A ferment is present in milk as well as in other vegetable and animal secretions which can reduce nitrates and chlorates in the presence of an oxidisable substance (salicylaldehyde, anisaldehyde). The ferment decomposes water with the liberation of hydrogen and hydroxyl ions, and thus has reducing as well as oxidising power. Oxyhydrase is a factor in the antitoxic defence of the organism, and is adapted to the anærobic life of the cells. H. W.

The Quantitative Excretion of Silicic Acid in Human Urine. M. GONNERNANN (*Biochem. Zeitsch.*, 1919, **94**, 163—173).—Normal human urine contains silica, the excretion of which may be raised by the ingestion of certain mineral waters. J. C. D.

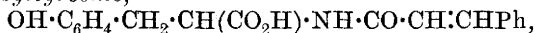
The Treatment of Wounds with the Carrel-Dakin Solution. K. ORTO (*Deut. med. Woch.*, 1917, **43**, 174—175; from *Chem. Zentr.*, 1919, i, 123).—The prescribed method of preparing the solution is too complicated for use in the field, and the following simpler process is recommended. Bleaching powder (200 grams) is

ground with water and addition of the latter is continued with constant stirring until the volume is 7 litres. A solution of sodium carbonate (140 grams) in water (2 litres) is added with stirring, and the solution is filtered. A solution of boric acid (40 grams) in water (1 litre) is added to the filtrate. Since this solution often causes a burning sensation it was later reduced to half strength and, in this form, rendered good service. Treatment with Dakin's solution has chiefly a prophylactic value.

H. W.

Behaviour of Cinnamic Acid and its Derivatives in the Animal Body. HIDEZO ANDO (*J. Biol. Chem.*, 1919, **38**, 7—11).— α -Benzoylaminocinnamic acid and *o*-benzoylaminocinnamic acid were recovered from the urine unchanged after subcutaneous or oral administration to dogs or rabbits. Only small amounts of α -benzoylamino-*p*-hydroxycinnamic acid could be so recovered. Administrations of cinnamoyltyrosine by the mouth were followed by the appearance of hippuric acid in the urine. The substance is apparently broken down by the animal organism.

Cinnamoyltyrosine,



was obtained as its *ethyl* ester (m. p. 130°) by the action of sodium carbonate on mixed solutions of cinnamoyl chloride and tyrosine ester in chloroform. On hydrolysis with sodium hydroxide, cinnamoyltyrosine was obtained, crystallising in polygonal prisms, m. p. 166—167°.

J. C. D.

Metabolism of the Furan and Hydrofuran Derivatives in the Animal Body. NOBUYOSHI SUZUKI (*J. Biol. Chem.*, 1919, **38**, 1—5).—Hydroxymethylpyromucic acid was isolated from the urine of rabbits which had received subcutaneous or oral administrations of chitose.

J. C. D.

Chemistry of Vegetable Physiology and Agriculture.

Absolute and Relative Disinfecting Power of Elements and Chemical Compounds. HANS FRIEDENTHAL (*Biochem. Zeitsch.*, 1919, **94**, 47—68).—An exhaustive study of the disinfecting powers of a large number of products. The relative disinfecting powers of the elements in each group of the periodic classification are given, as well as information regarding many organic disinfectants. [See further, *J. Soc. Chem. Ind.*, 1919, July.] J. C. D.

The Effects of Acids, Alkalis, and Sugars on the Growth and Formation of Indole by *Bacillus coli*. FRANK JOHN SADLER WYETH (*Biochem. J.*, 1919, **13**, 10—24).—The activity of

B. coli in 2% peptone is determined by almost the same initial conditions of acid and alkaline reactions as is the case when fermentation is conducted in 2% dextrose peptone. The approximate limits of initial reaction are $p_H=4.27$ to 9.87 . A change of the initial reaction of the medium results in a change, similar in direction, but smaller in magnitude, in the final reaction of the culture. For *B. coli* grown in 2% dextrose peptone, whilst the initial reactions of the media vary from $p_H=4.30$ to 9.82 , the final reactions only vary between $p_H=4.27$ and 4.82 . When grown in 2% peptone the initial reaction may be from $p_H=4.30$ to 9.37 , and the final reaction from $p_H=5.92$ to 8.55 .

The proteolytic fermentation resulting in the peptone medium causes an increase of final alkalinity, unless the initial reaction lies between $p_H=9.37$ and 8.48 , in which case the final reaction is less alkaline than the initial reaction. The saccharolytic fermentation of *B. coli* in 2% dextrose peptone produces approximately constant amounts of acids and no appreciable amount of ammonia; on the other hand, when in a peptone medium the organism produces ammonia and acids in increasing amounts as the initial reaction of the medium increases in alkalinity. Formation of indole is retarded by the presence of free alkali or acid, whilst certain sugars also inhibit the formation of this substance by depressing the proteolytic activity of the bacillus.

J. C. D.

The Action of Electrolytes on the Electrical Conductivity of the Bacterial Cell and their Effect on the Rate of Migration of these Cells in an Electric Field. C. SHEARER (*Proc. Cambridge Phil. Soc.*, 1919, **19**, 263—266).—A thick, creamy emulsion of the meningococcus or *B. coli* in neutral Ringer's solution (that is, one in which the sodium hydrogen carbonate is left out) has a resistance, as measured by electrical conductivity determinations, more than treble that of the same solution without the bacteria. If in place of Ringer's solution the emulsions are prepared with a solution of sodium chloride having the same conductivity as the Ringer's solution, a high resistance is obtained at first, but this rapidly drops, and at the end of thirty to forty minutes is the same as that of the saline solution alone. Further, it is found that immersion in such a solution for several hours kills the bacteria. If, when the resistance of such an emulsion in sodium chloride solution has dropped to normal, a little calcium chloride is added, the bacterial emulsion regains its high resistance and the bacteria are uninjured. Potassium, lithium, and magnesium chlorides act like sodium chloride, whilst barium and strontium chlorides act like calcium chloride. These results agree with those obtained by Loeb, Osterhout, and others with animal and plant cells.

The positive tervalent ions of lanthanum nitrate, and cerium and neo-ytterbium chloride and the negative tervalent ions of sodium citrate appear to have no action in increasing or decreasing the resistance of the bacterial cell as determined by the conductivity method when used in very dilute solutions. On the other hand,

these salts and especially lanthanum nitrate, have a marked action in changing the rate of migration of these bacterial cells in an electric field. The addition of the lanthanum nitrate reduces the rate of migration, or, in other words, considerably alters the nature of the electrical charge on the bacterial cell wall. W. G.

Decomposition of Betaine by the Bacteria of "Guanol," a Fertiliser Prepared from Molasses Waste. ALFRED KOCH and ALICE OELSNER (*Biochem. Zeitsch.*, 1919, **94**, 139—162).—Organisms were found which attack betaine with the formation of trimethylamine, ammonia, and carbon dioxide. Methyl alcohol, formic acid, and acetic acid in small amounts appear to be the intermediate products in the production of carbon dioxide. [See further, *J. Soc. Chem. Ind.*, July, 1919.] J. C. D.

Action of Mixtures of Certain Salts on the Lactic Acid Fermentation. CHARLES RICHET and HENRY CARDOT (*Compt. rend. Soc. Biol.*, 1918, **81**, 751—755; from *Chem. Zentr.*, 1919, i, 380).—The action of combinations of antiseptic salts on the lactic acid fermentation has been examined. Action is not additive; the more potent salt (copper sulphate) behaved after addition of cadmium sulphate as if the latter were not present. Addition of the sulphates of copper or zinc did not modify the antiseptic action of cadmium sulphate. H. W.

Fumaric Acid Fermentation of Sugar. C. WEHMER (*Ber.*, 1919, **52**, [B], 562—564).—A reply to Ehrlich (this vol., i, 239) denying that *Rhizopus nigricans* produces fumaric acid. J. C. W.

Influence of Varying Barometric Height on the Course of Alcoholic Fermentation and on Biological Processes in General. AUGUST RIPPEL (*Centr. Bakt. Par.*, 1917, [ii], **47**, 225—229; from *Chem. Zentr.*, 1919, i, 34).—The curves showing loss in weight due to the escape of carbon dioxide during slow fermentation show distinct zig-zags due to variations in the atmospheric pressure, the curve sinking with rising pressure and rising with decreasing pressure. The natural effect of change of pressure on the evolution of carbon dioxide must affect the course of fermentation in proportion as the yeast is influenced by the degree of saturation of carbon dioxide. The same considerations also apply to other biological processes in which a gas is evolved (ammonia, hydrogen sulphide, etc.), and a similar influence must also be operative in nature. H. W.

Ferment Action. IV. Further Studies on the Adsorption of Mixtures of Amino-acids with Polypeptides and Other Substances. Behaviour of Amino-acids and Polypeptides towards Albumin Solutions, Blood-Serum, and during the Coagulation of Sols. EMIL ABDERHALDEN and ANDOR FODOR (*Fermentforsch.*, 1918, **2**, 211—224; from *Chem. Zentr.*, 1919, i, 95—96. Compare A., 1917, i, 306; 1919, ii, 49, 50).—The previous

observation that the presence of carbohydrates diminishes the adsorptive power of animal charcoal towards polypeptides, and that conversely the adsorption of carbohydrates is adversely influenced by polypeptides, whilst in the presence of amino-acids the displacement of adsorption is one-sided, is confirmed by further examples. Thus the behaviour of proline is similar to that of other amino-acids, whilst glycine anhydride and pyrrolidonecarboxylic acid behave like dextrose. It is found that amino-acids and polypeptides can, in certain circumstances, be completely displaced by other amino-acids or higher polypeptides without the latter suffering displacement, but that the greater number only cause partial displacement.

The behaviour of various sols in this connexion has also been investigated with the possible aim of measuring the rate of adsorption and investigating its degree of dependence on the hydrogen-ion concentration of the solution. The sols investigated (ferric hydroxide, aluminium hydroxide, and arsenic sulphide) did not, however, adsorb amino-acids and polypeptides during coagulation. On the other hand, glycyl-*l*-leucine was adsorbed by coagulating blood serum.

H. W.

Ferment Action. V. Ultrafiltration Experiments with Mixtures of Amino-acids or Polypeptides with Yeast Juice. Evidence for the Colloidal Condition of Ferments and Extension of the Adsorption Theory. EMIL ABDERHALDEN and ANDOR FODOR (*Fermentforsch.*, 1918, 2, 225—250; from *Chem. Zentr.*, 1919, i, 96. Compare preceding abstract).—The quantity of water employed in the maceration of yeast has great influence on the activity and stability of the juice. When ten times the amount of water is used, a stable juice, which is immediately active, is obtained; when three times the quantity of water is used, the initial activity of the juice is slight, but increases rapidly on keeping, and finally reaches a maximum which is never attained in the former case. Difference appears to depend on an alteration in the state of the ferment, for example, its dispersivity with dilution. In this connexion, a series of ultra-filtration experiments have been performed. The extracts, obtained from various dried yeasts, had very differing activities towards glycyl-*l*-leucine. Yeast juices mixed with the latter or with *l*-leucine yielded filtrates which were always poorer in amino-nitrogen than the original mixtures, the loss being relatively greater from dilute than from concentrated solution. The originally inactive yeast juices also had power of adsorption, and the equilibrium is independent of the amount of hydroxyl ions present. Adsorption occurs with polypeptides (glycyl-*d*-leucine) which are not attacked by yeast juice. Under equivalent conditions, the adsorption of a complex polypeptide is greater than that of a dipeptide. With decrease in the fermentive activity of a juice by age or by heat a decrease in adsorptive capacity is observed which may sink to zero. Considered in connection with the observation that adsorption can occur with inactive juices, this leads to the deduc-

tion that whilst adsorption of the substrate by the colloidal ferment precedes fission, the latter process does not necessarily follow the former. Further evidence is shown by the behaviour of glycyl-L-leucine, which, at 0°, is adsorbed by yeast extract, but not decomposed.

The temperature-coefficient of fission of polypeptides generally lies between 1.3 and 2.4 according to conditions (yeast extract, temperature, hydrogen-ion concentration, and substrate). The optimum temperature for $p_H = 7.50$ is between 50° and 55°.

The chief results of the work in this field are collected and reviewed. H. W.

The Nitrogenous Constituents of Yeast. JAKOB MEISENHEIMER (*Zeitsch. physiol. Chem.*, 1919, **104**, 229—283).—An investigation of the nature of the monoamino-acids present in the products of autolysis derived from bottom and top fermenting yeasts. The estimations were carried out by the ester method of Fischer. Glycine, alanine, valine, leucine, proline, phenylalanine, aspartic and glutamic acids, tyrosine, and tryptophan were identified. Serine and cystine were recognised with less certainty, and there was also evidence of the presence of an aminobutyric acid. Glucosamine was isolated from the cell residue of the autolysis. J. C. D.

Enzymatic Power of Yeast. TH. BOKORNY (*Allgem. Brau.-Hopf. Zeit.*, 1918, **58**, 1093—1094; from *Chem. Zentr.*, 1919, i, 96—97).—Experiments are described on the inhibiting action of disinfecting agents, even in minute quantity, on the fermentative activity and other enzymatic powers of yeast. Formaldehyde (0.2%) retards growth and fermentation, the yeast is killed, as is also the fermentation ferment; 0.05% does not destroy the activity of the latter. 0.1% Kills zymase within two days, but 1% does not render invertase inactive in the same time, sugar solution being strongly inverted. It is therefore possible with the aid of formaldehyde to prepare a yeast which can invert, but not ferment, sugar. Phenylhydrazine (0.5%) inhibits the fermentation of maltose, but not of dextrose. Fermentation persists slightly in the presence of mercuric chloride (0.02%), but is inhibited by 0.1%, although sucrose is still powerfully inverted. The action of silver nitrate is similar. Alcohol (10%) does not cause a permanent inactivity of zymase within five days, and, even after twenty days, slight fermentative power persists. Absolute alcohols destroy the power to ferment within ten minutes. H. W.

Alterations in the Metabolism and Cellular Permeability at Temperatures near the Freezing Point. E. PANTANELLI (*Atti R. Accad. Lincei*, 1919, [v], **28**, i, 205—209).—When cooled to a temperature closely approaching the freezing point, the endocarp cells of the almond exhibit a progressive increase of the cellular permeability, which is rendered evident by rapid emission of water from the tissue in a dry atmosphere and by exosmosis of substances

from the tissue immersed in water. This phenomenon is accelerated by the presence of certain compounds which penetrate rapidly into the cell, such as glycerol, ethyl alcohol, citric acid, and free alkali. Such increase in cellular permeability is accompanied by rapid destruction of the sugars; this effect may be restricted by supplying either substances capable of being absorbed and utilised for the respiration, for instance, glycerol, ethyl alcohol, or citric acid, or substances which retard the exosmosis of the sugars, or intermediate products of the respiration, such as sodium chloride, potassium phosphate, and citric acid. Sugars (sucrose, dextrose) present in the external liquid do not exert a similar restricting action, since they are not absorbed. A further phenomenon caused by the low temperature is intense auto-digestion of the proteins, this being enhanced by exosmosis of the soluble products of the digestion and by rapid destruction of the sugars. T. H. P.

Influence of Fluorides on Vegetation. A Preliminary Experiment in Flower Pots. ARMAND GAUTIER and P. CLAUSMANN (*Compt. rend.*, 1919, 168, 976—982).—As the result of pot trials, using wood charcoal to which the necessary nutrients had been added as a culture medium, the authors find that fluorine in the form of potassium fluoride exerted a favourable influence on the growth of seven species of plants, had no effect on three, and caused a lower crop yield in the case of three. W. G.

Comparative Rate of Absorption of Various Salts by Plant Tissue [Carrot and Potato]. WALTER STILES and FRANKLIN KIDD (*Proc. Roy. Soc.*, 1919, [B], 90, 487—504).—The rate of absorption of various chlorides, sulphates, nitrates, and potassium salts from solutions of 0.02*N*-concentration was measured by the electrical conductivity method. A rapid withdrawal of salt from solution occurred during the first few hours, after which the absorption proceeded to an equilibrium over a period of several days, the curve being approximately logarithmic in the latter case. Cations were absorbed in the orders K, Ca or Na, Li, Mg or Zn, Al, and K, Na, Li, Ca, or Mg, and anions in the orders SO₄, NO₃, Cl, and NO₃, Cl, SO₄, during the initial and equilibrium periods respectively, these results being generally in agreement with those obtained by Ruhland, Fitting, Pantanelli, and Troendle, who failed to differentiate between the initial and equilibrium stages. The rate and extent of intake of one ion of a salt were found to be influenced by the nature of the other ion, and, as previously observed by Rothert and Meurier in the case of aluminium sulphate, aluminium was absorbed much more rapidly than its anion. According to Troendle, the rate of absorption of the metallic ions in any group of the periodic classification increases with the atomic weight. It is pointed out that although this view is not contradicted by the present results, the latter show equally that the initial rate of absorption is largely dependent on the mobility of the ions or diffusibility of the salt, and that the

position of equilibrium appears to be governed by some quite different property, since at this stage the bivalent ions, Ca, Mg, SO_4 , are absorbed to a much smaller extent than the univalent ions, K, Na, Cl, NO_3 .

W. E. F. P.

Fatty Oil from the Seeds of the Evening Primrose [*Oenothera biennis*], and a New Linolenic Acid. A. HEIDUSCHKA and K. LÜFT (*Arch. Pharm.*, 1919, 257, 33—69).—The air-dried seeds of the evening primrose contain water (13·95%), crude proteins (13·38%), fat (16·93%), fibre (14·56%), nitrogen-free extractives (35·03%), and ash (6·15%). The oil was obtained by extraction of the crushed seeds with ether, and formed a golden-yellow substance resembling poppy oil in taste and odour; it remained completely liquid at 0° , but a few solid particles separated at -11° . It had D_{15}^{20} 0·9283, n_D^{20} 1·4722, acid number 0, saponification number 195·2, Reichert-Meissel number 2·61, Polenski number 0·57, iodine number 148·92, Hefner number 94·94, acetyl number 13·9. It was optically inactive and a member of the class of drying oils. The volatile fatty acids consisted mainly of hexoic acid (0·81%). Separation of the unsaturated and saturated fatty acids was effected in the usual manner by means of the lead salts, and the former were brominated in glacial acetic acid—ethereal solution. Under these conditions, a sparingly soluble *hexabromo- γ -linolenic acid*, microscopic needles, m. p. 195—196° (decomp.), separated which, when treated with zinc and alcohol, yielded *γ -linolenic acid* as a yellow substance of unpleasant odour. Tetra-bromo- α -linoleic acid, tetrabromo- β -linoleic acid, and dibromo-oleic acid were identified in the filtrates from hexabromo- γ -linolenic acid. The unsaturated fatty acids contain *γ -linolenic acid* (2·50%), α -linoleic acid (30·20%), β -linoleic acid (38·11%), and oleic acid (29·19%). Oxidation of the unsaturated fatty acids with permanganate yielded dihydroxystearic acid, a mixture of tetrahydroxystearic acids, and *γ -hexahydroxystearic acid*, minute needles, m. p. 245° (decomp.).

Fractionation of the saturated fatty acids from alcohol or by means of their magnesium salts led to the isolation of palmitic acid and a substance the properties of which agree with those of daturic acid; theoretical considerations caused the authors to doubt the natural occurrence of the latter acid, and experiments on the fractional distillation of the substance with steam showed that the "daturic acid" obtained from the evening primrose, at any rate, was a mixture of palmitic acid (and possibly stearic acid) with acids of greater molecular weight.

The unsaponifiable matter of the oil contained phytosterol (2·27%), the acetate of which had m. p. $130\cdot3^\circ$ (corr.). H. W.

Investigations on the Anthocyanin Metabolism on the Basis of the Chemical Properties of the Anthocyanin Group.

K. NOACK (*Zeitsch. Bot.*, 1918, 10, 561—628; from *Physiol. Abstr.*, 1919, 4, 99).—A study of *Polygonum compactum* and various

Paeonia species and varieties. In the first days, leaves of *Polygonum compactum* have an intense red coloration, which fades away in the following days, and the leaves finally become green. The following explanation of this phenomenon is suggested. Anthocyanin is dissociated by means of an enzyme into anthocyanidin and sugar. The anthocyanidin is isomerised into a colourless pseudo-base, and this, during its oxidation, can become transformed into a yellow pigment which, by photochemical reduction, may again give the pseudo-base of anthocyanidin. The amounts of anthocyanidin and its oxidation product vary inversely with one another. The variations are influenced by light, since the pseudo-base is formed by photochemical reduction of the oxidation product of the pigment. In the dark, anthocyanidin is again oxidised, this process being accelerated by heat, light and temperature thus having an antagonistic action. An oxidation product of anthocyanidin, but not anthocyanidin itself, is found in the vegetative organs of various *Paeonia*, and the amount of this oxidation product varies directly with the amount of anthocyanin in the plant. In the flowers, in addition to the oxidation product, the anthocyanidin pseudo-base may occur, but only in small quantities, and without any relation to the amount of anthocyanin formed in the development of the flower.

W. G.

Occurrence of Vanillin. EDMUND O. VON LIPPMANN (*Ber.*, 1919, 52, [B], 905).—The occasional presence of vanillin in potato tubers, particularly in the layers immediately beneath the skin, has been frequently observed. It is now found that vanillin can also be extracted from the fresh, blue blossoms (but not from the white ones); it disappears fairly rapidly from the plucked flowers.

H. W.

Preparation of Sucrose from Plants. E. WINTERSTEIN (*Zeitsch. physiol. Chem.*, 1919, 104, 217—219).—The ether extracted fruits of *Sapindus utilis* were extracted with boiling alcohol in the presence of potassium carbonate. The filtered extract, after concentration, was treated with freshly precipitated lead hydroxide for six days. From the lead-free filtrate, a fraction was obtained by extraction with methyl alcohol, which gave sucrose on crystallisation.

J. C. D.

The Protein Extract of Ragweed Pollen. FREDERICK W. HEYL (*J. Amer. Chem. Soc.*, 1919, 41, 670—682. Compare A., 1917, i, 618).—Three large samples of ragweed pollen have been percolated with ether and 95% alcohol (loss in weight, about 22%), and the residue examined for proteins by repeated macerations with (a) water, (b) 10% salt solution, (c) 0.2% potassium hydroxide. The aqueous extract was found to contain an albumin (1.2%), coagulating at about 45—50°, and proteoses (3%), and when partly saturated with ammonium sulphate gave a precipitate consisting of albumin and proteose in the proportion 3:1, and causing

anaphylaxis in guinea-pigs. After precipitating all the protein from this extract by means of ammonium sulphate, and then removing the sulphate, phosphotungstic acid gave a precipitate of the following bases: adenine, guanosine (?), histidine, arginine, lysine, and agmatine, these being identified by the usual methods. The 10% salt extract gave a small amount of the above albumin and but very little evidence of the presence of a globulin. The dilute alkali extract contained the chief protein, which is therefore a glutelin, amounting to about 2.9% of the weight of the pollen, and appearing as an almost white, dusty powder. J. C. W.

A Proximate Analysis of *Rumex crispus*, and a Comparison of its Hydroxymethylantraquinones with those from Certain Other Drugs. GEORGE D. BEAL and RUTH E. OKEY (*J. Amer. Chem. Soc.*, 1919, **41**, 693—706).—An examination of the extract made by percolating the dried and powdered root of the common yellow (curled) dock with cold 95% alcohol. The constituents which are soluble in water, yielded small quantities of emodin, a mixture of emodin monomethyl ether and chrysophanic acid, dextrose and a little levulose, and organic acids and much resinous material. The insoluble portion of the extract contained emodin, its monomethyl ether, chrysophanic acid, a phytosterol, palmitic, stearic, and erucic acids with lower unsaturated and higher saturated fatty acids, a small amount of a hydrocarbon, an essential oil, some glucosides, and much resin.

A cursory examination of cascara and aloes has also been made, mainly with the aim of isolating their emodins. *Rumex* emodin is identical with that of cascara (Jowett, A., 1905, ii, 192) and isomeric with the aloes-emodin of aloes and senna. The phytosterol is also the same as the "rhamnol" of cascara.

The yield of emodin from the dried dock root is about 0.1%, and that of chrysophanic acid somewhat less. This compares favourably with the quantities obtainable from more expensive drugs.

J. C. W.

Toxicity of "Alkali" Salts. THAKUR MAHADEO SINGH (*Soil Sci.*, 1918, **6**, 463—477).—An examination of the effect of various sodium salts on ammonifying, nitrifying, and nitrogen-fixing organisms, and on the germination and growth of wheat and peas. Arranged in order of descending toxicity, the salts examined are sodium chloride, nitrate, carbonate, and sulphate, the percentage of the anion, and not of the cation, being the determining factor. Small amounts of each of the different salts used stimulated both crop growth and bacterial activity, the amount varying with the crop grown. The toxicity point as found when salts were used in combination, as under field conditions, agreed very closely with the points found when the individual salts were used. The toxic point of the combined salts depended on the percentages of the chlorides, nitrates, carbonates, and sulphates present, and the combination in which they existed. Calcium sulphate when present

lowered the toxic point of the chloride, carbonate, or nitrate of sodium.

W. G.

Alfalfa [Lucerne] Investigation. VII. Alfalfa Saponin. C. A. JACOBSEN (*J. Amer. Chem. Soc.*, 1919, **41**, 640—648).—When alfalfa hay is extracted with hot alcohol and the solution is cooled, a voluminous, green precipitate is deposited, from which ether extracts two ketones, myristone and alfalfone (A., 1912, ii, 80; i, 239). The insoluble, gummy residue left in the Soxhlet thimble contains a saponin, which may be isolated by dialysis of the aqueous solution and reprecipitation with alcohol. Alfalfa [lucerne] saponin, $C_{27}H_{37}O_{16}N$, is a brown, amorphous powder, decomp. $280-300^{\circ}$, readily soluble only in water and glycerol, and may be hydrolysed to a sapogenin, $C_{18}H_{18}O_{10}N$, dextrose, and a pentose. It also forms an acetyl derivative, but this may be the acetate of the sapogenin. Its solution has an enormous surface tension, minute quantities producing a remarkable foam in aerated beverages, and bubbles 4 inches in diameter being possible with a 25% solution.

The saponin differs from most compounds of this type in containing nitrogen. It is also abnormal in that it does not hæmolyse blood. It is toxic to fish, but this generally accepted property of saponins as a class seems to be due to their power of preventing the diffusion of air into the water, for the golden carp, which has the instinct to rise to the surface to breathe, will live in saponin solutions (1 to 35,000), whereas the black bass succumbs. Alfalfa saponin causes acute local irritation and death when injected subcutaneously, but is harmless when taken *per os*.

The crude saponin is accompanied by a yellow substance, "saponin X," and alfalfa also contains two proteins and a bitter principle, which are being investigated.

J. C. W.

Effect of Manganese on the Growth of Wheat. A Source of Manganese for Agricultural Purposes. J. S. MCHARGUE (*J. Ind. Eng. Chem.*, 1919, **11**, 332—335).—Results of pot cultures showed that the addition of manganese increases the size and nitrogen content of wheat grains, and stimulates the growth of the plant; the most favourable quantity appeared to be about 0.028% of manganese, calculated on the total weight of the soil in the pot. It was added in the form of manganese carbonate. Basic slag contains an average of 4.8% of manganese, and it is possible that some of the benefit to crops resulting from the use of this fertiliser is due to the presence of manganese.

W. P. S.

Solubility of the Calcium, Magnesium, and Potassium in such Minerals as Epidote, Chrysolite, and Muscovite, especially in regard to Soil Relationships. R. F. GARDINER (*J. Agric. Res.*, 1919, **16**, 259—261).—When the finely powdered minerals were left in contact with the aqueous extract from an acid soil for two months at 25° , it was found that 1.6% of the total calcium in the epidote, 0.21% of the magnesium in the

chrysolite, and from 11 to 21% of the potassium in the muscovite was extracted under the experimental conditions. W. G.

Decomposition of Cyanamide and Dicyanodiamide in the Soil. G. A. COWIE (*J. Agric. Sci.*, 1919, **9**, 113—136).—Experiments on field plots and on soil in pots show cyanamide to be decomposed in soil, yielding ammonia, which is then nitrified in the usual way. The conversion of the nitrogen of the cyanamide into nitrate is almost quantitative. Dicyanodiamide undergoes no decomposition. On adding both substances together to soil, it is found that the dicyanodiamide does not prevent the formation of ammonia from the cyanamide, but that it largely prevents nitrification. In a mixture of the two substances containing 25% of dicyanodiamide, only 22% of the nitrogen is converted into nitrate, and in a mixture containing 75% of dicyanodiamide, only 5%. Dicyanodiamide is thus toxic to the nitrifying organisms. On the ammonifying bacteria it has no effect, as dried blood readily undergoes ammonification in its presence, and the ammonia produced accumulates in the soil owing to the action of the nitrifying organisms being prevented. These results show that cyanamide is not normally converted into dicyanodiamide in soil; they also suggest the possibility of a di-imino-formula for dicyanodiamide. [See also *J. Soc. Chem. Ind.*, 1919, 380A.] J. H. J.

Soluble Non-protein Nitrogen of Soil. R. S. SNYDER and R. S. POTTER (*Soil Sci.*, 1918, **6**, 441—448).—From a further study of the method previously described (A., 1917, i, 75), the authors find that, in order to obtain the maximum soluble non-protein nitrogen from basic soils, they should be extracted with 1% hydrochloric acid until the washings show no calcium. It is unnecessary to extract acid soils with the acid. Nitrates in the acid extract may be reduced by Devarda's alloy after making the extract faintly alkaline. The examination of a number of soils shows that the amount of the unknown soluble non-protein nitrogen is usually decreased by an application of lime, although there are exceptions. W. G.

Manuring Experiments with "Kalikalk." H. G. SÖDERBAUM (*Medd. No. 163, Centralanstalten försöks. jordbruk; from Bied. Zentr.*, 1919, **48**, 135—136).—This preparation (prepared by heating together potash felspar, limestone, and gypsum at 1150°) gave good results in the manuring of oat crops. [See further, *J. Soc. Chem. Ind.*, 1919, July.] J. C. D.

Organic Nutrients for Green Plants. TH. BOKORNY (*Biochem. Zeitsch.*, 1919, **94**, 78—83).—Sulphite lye from the cellulose industries, even after the removal of the majority of the sugar, is of considerable value as a manure. The value of human urine as a nutrient for plants is also great. The presence of hippuric acid in the urine of certain domestic animals makes this waste product less useful than human urine. This may be due to the toxic influence of the benzoic acid. J. C. D.

Organic Chemistry.

The Atom Model of Rutherford and Bohr in Chemistry.

A. E. LACOMBLE (*Chem. Weekblad*, 1919, **16**, 832—834).—A discussion of various difficulties which arise in the further development of the ideas suggested by Buchner (this vol., i, 245) in his application of the Rutherford-Bohr theories of atomic structure to the case of atom linking in organic compounds. If the single bond between two carbon atoms be constituted by the attraction of two valency electrons revolving in an orbit perpendicular to the line joining the two positive nuclei, then, in addition to the electrostatic field, an electromagnetic field is established the direction of which is determined by the sense of the motion of the electrons in the orbit. In the case of the methane molecule there would thus be several possible isomerides owing to the possibility of positive or negative rotation of the electrons in the four atomic bonds as viewed from the carbon nucleus. Two of these isomerides are symmetrical, the rotations in one being all positive and in the other all negative. These are enantiomorphous isomerides, and each gives rise to one derivative of the formula CH_3R and one CH_2R_2 . The unsymmetrical possibilities may be represented as $+++$, $++-$, $+--$, $---$. Each of these gives two isomeric mono-derivatives of the formula CH_3R . As these are unknown, it may be assumed that only the symmetrical forms exist. In chains of carbon atoms "positive" carbon atoms must alternate with "negative" atoms, so that a closed ring is only possible with an even number of atoms, unless for the odd atom an abnormal structure is assumed, which would again render possible the existence of unknown isomerides. It is also pointed out that the displacement of the electrons to form orbits between the carbon atoms of the diamond would probably be indicated in the Röntgen diagram of the crystal by the presence of lines. Such lines have not been observed. W. S. M.

The Nature of the Ethylenic and Acetylenic Linkings in Carbon Compounds. W. E. GARNER (*Chem. News*, 1919, **119**, 16—17).—The appearance or disappearance of the unsaturated linking in carbon compounds is generally accompanied by *trans*-elimination or *trans*-addition of the groups leaving or entering the molecule. An explanation of the mechanism of such reactions is offered in terms of Bohr's theory of the arrangement of the atoms and electrons in the molecule. It is shown by means of diagrams that when two univalent atoms, for example, hydrogen and bromine, become detached from two adjacent carbon atoms, with formation of an ethylenic linking, this is more likely to occur in the *trans*- than in the *cis*-position. E. H. R.

New Practical Method of Carbonising Coal at Low Temperatures. FRANZ FISCHER and W. GLUUD (*Ber.*, 1919, **52**, [B], 1035—1039).—Difficulties are encountered in carbonising

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considerable quantities of coal at low temperatures in a reasonable time since, owing to the low thermal conductivity of the material, the heat penetrates so slowly into the interior of the charge that the outer portions readily become overheated. The authors consider that the conditions essential for success are that the volatile portions should not be heated to a temperature higher than that necessary for their volatilisation and that they should not be exposed to this temperature for an unnecessarily long period. They have therefore constructed a cylindrical retort which can be rotated round a horizontal axis. The latter is hollow, but is plugged in the middle. Through the one end steam is admitted which carries off the volatile products through the other end to a suitable condensing arrangement. The furnace is heated from underneath by a series of gas burners fed with air under pressure, whilst loss of heat is prevented by enclosing the furnace with a metal sheath. A thermo-couple is placed in the axis. The furnace permits the distillation of 20 kilos. of coal in one to two hours. Distillation generally commences at about 350° and is complete at 500° . The yield of tar is 3--30%, according to the kind of coal used. The first portions of the oils are lighter than water, the last portions are heavier, the mean density being slightly greater than unity. The tar appears in thin layers as a golden-red oil, which is more or less viscous according to the kind of coal used. H. W.

Paraffin from Coal. W. GLUUD (*Ber.*, 1919, 52, [B], 1039—1053).—The occurrence of paraffin in low-temperature tars has been frequently noted, but little is known as to the nature of the individual components. The author has therefore investigated the tar derived from a Mond gas plant fed with a gas coal and finds the paraffin to be a mixture of saturated normal paraffins terminating with $C_{29}H_{60}$, in which hexa- and hepta-cosane preponderate. The series thus appears to be less comprehensive than with brown coal paraffins.

[With FRL. HENNY HÖVERMANN.]—The paraffin exists as such in the crystalline state in the tar, from which it is isolated by treatment of the latter with acetone; in the earlier experiments attempts were made to isolate a pure product by repeated crystallisation of the crude substance, first from acetone and subsequently from benzene. In this manner, heptacosane was ultimately isolated. Better results, however, were obtained by repeated fractional distillation of the crude product under diminished pressure and crystallisation of the individual fractions when necessary. The complete series from $C_{24}H_{50}$ to $C_{29}H_{60}$ could thus be isolated, the identity of the products being established by direct comparison with the synthetic substances. Heptacosane was prepared by the action of phosphorus pentachloride on myristone and treatment of the chloride with hydriodic acid; contrary to the usual assumption, however, the intermediate product was found to be *vxx-trichloro-n-heptacosane*, needles, m. p. about 30° , the formation of which is attributed to the ketone reacting in its enolic form and addition of

chlorine occurring at a higher temperature. Octacosane was prepared in satisfactory yield by the electrolysis of a mixture of myristic and palmitic acids. The following constants are recorded for the synthetic hydrocarbons: $C_{26}H_{54}$, n_D^{25} 1.43332, n_C^{65} 1.43096, n_F^{65} 1.43851, n_D^{80} 1.42774, n_C^{80} 1.42534, n_F^{80} 1.43293; $C_{27}H_{56}$, n_D^{65} 1.43453, n_C^{65} 1.43228, n_F^{65} 1.43992, n_D^{80} 1.42874, n_C^{80} 1.42636, n_F^{80} 1.43411; $C_{28}H_{58}$, n_D^{65} 1.43539, n_C^{65} 1.43309, n_F^{65} 1.44071, n_D^{80} 1.42971, n_C^{80} 1.42737, n_F^{80} 1.43501.

Investigation of the paraffins obtained from other varieties of coal rendered it very probable that they are closely similar in composition. The isolation of small amounts of paraffin by the direct extraction of coal with benzene at 260—270° leads the author to the conclusion that it exists in all probability to some extent as such in coal, and is therefore not exclusively a product of secondary processes occurring during distillation. H. W.

Light Petroleum from Coal. FRANZ FISCHER and W. GLUUD (*Ber.*, 1919, **52**, [B], 1053—1068).—The object of the investigation was to get a general insight into the nature of the most volatile fractions of low-temperature tar. It was found that considerable quantities (about 1% of the weight of the coal) of light petroleum could be obtained, and that benzene is not present in more than minimal amount.

Three different coals were investigated, a gas coal (Zecke Lohberg) and two fat coals (Flöz Albert and Minden). The latter was of interest, since the mine from which it was obtained was known to smell of petroleum; the coal evolved paraffins at a temperature well below that at which carbonisation commenced, so that it is established that light paraffins can exist pre-formed in certain coals. The light petroleum was isolated from the gas and also from the tar. In the former case, since it was desired to operate in a technical manner, extreme cooling as with liquid air was not adopted; the products were isolated either by liquefaction by compression in steel cylinders or, preferably, by compression into paraffin oil and isolation from the latter by treatment with steam. In this manner the considerable fraction boiling below 20° was lost; the product had b. p. 20—100° with only small portions of higher boiling point. The tar was treated with steam and the distillation was discontinued when only small quantities of oil came over, since otherwise considerable quantities of phenolic substances distilled. The boiling point of the distillate was mainly 60—200°. All the fractions contained sulphur compounds. They were purified by treatment with alkali and then with concentrated and 15% fuming sulphuric acid or, preferably, with aluminium chloride; the use of liquid sulphur dioxide proved less advantageous. Perfectly colourless liquids were thus obtained, which were stable towards light and air. The fraction, b. p. 20—60°, was composed of saturated paraffin hydrocarbons; that of b. p. 60—100° contained naphtheues mixed in the case of the gas coal with paraffins. The composition of the higher fractions, b. p.'s 100—125° and 125—190°, was less definite; they

appeared to be mixtures of paraffins with naphthenes with higher hydrogen content and, probably, complex aromatic compounds.

The fractions, b. p. 60—100°, were examined for benzene; the presence of the latter in small amount was established in a product obtained from the Minden coal and purified with liquid sulphur dioxide, the isolation being directly effected by exposure to low temperature, but the quantity present cannot exceed 3%. The fractions obtained from the second fat coal and from gas coal and purified by aluminium chloride appeared to be free from benzene when examined by the triphenylmethane method. The usual identification by successive conversion into nitrobenzene and aniline appeared inadmissible in this instance owing to the danger of the formation of benzene by the oxidation of more highly hydrogenated products.

The behaviour of the several fractions when cooled has also been fully investigated; the original paper must be consulted for details.

H. W.

Preparation of some Volatile, Saturated Acyclic or Cyclic Hydrocarbons contained in Light Petroleums.

G. CHAVANNE and L. J. SIMON (*Compt. rend.*, 1919, 168, 1324—1326).—A number of aliphatic and cyclic hydrocarbons have been prepared and their b. p.'s, densities, and critical temperature of solution in aniline determined. The following results were obtained:

	Crit. temp. sol. in aniline.	B. p.	Density.
Pentane	72.0°	36.3°	D ₀ ⁴ 0.6454
isoPentane	77.0	28.0	D ₀ ⁴ 0.6394
isoHexane.....	73.8	61.7—62.4	D ₁₅ ⁴ 0.658
isoHeptane	72.8	90—91	D ₁₅ ⁴ 0.6842
Heptane... ..	70.0	98—98.3	D ₁₅ ⁴ 0.6879
Octane	71.8	125.8	D ₁₅ ⁴ 0.7063
Methylcyclohexane	41.0	100.4	D ₀ ⁴ 0.780
1:2-Dimethylcyclohexane ...	42.1	128.6—129	D ₁₅ ⁴ 0.798
1:3-Dimethylcyclohexane ...	49.7	121.2—121.8	D ₁₅ ⁴ 0.775
1:4-Dimethylcyclohexane ...	48.0	122.7—123	D ₁₅ ⁴ 0.783
cycloPentane	18.0	49.5	D ₁₅ ⁴ 0.750
Methylcyclopentane.....	35.0	72.0	D ₁₅ ⁴ 0.753

The authors find that, for the conversion of butyric, adipic, or methyladipic acid into its corresponding ketone, manganous carbonate is a very effective catalyst.

W. G.

Decomposition of Acetylene at High Temperatures in the Presence of Various Catalysts.

SIEGFRIED HILPERT (*Ges. Abhand. Kennt. Kohle*, 1917, 1, 271—275; from *Chem. Zentr.*, 1919, i, 709—710).—Experiments were undertaken with the object of polymerising acetylene to benzene, but a relatively satisfactory yield of the latter could not be obtained. In all cases, primary decomposition appears to involve the separation of carbon, and the formation of tar or benzene appears to be a secondary change. The acetylene was prepared from calcium carbide and purified by

passage over a long layer of kieselguhr impregnated with a solution of cuprous chloride in hydrochloric acid. The furnace consisted of an electrically heated Jena-glass tube. With coke as catalyst, it was found that the impurities in the material, particularly sulphur, took part in the change. With glass splinters, a fog of tar appeared at 400°, whilst at 500° a layer of carbon was slowly formed on the glass and a mixture of benzene and tar containing unsaturated substances was obtained; the decomposition of acetylene on glass appeared to be characterised by the formation of carbon at a relatively high temperature and the simultaneous production of tar. With powdered iron and more markedly with nickel, decomposition commenced at 300° and proceeded so rapidly at 400° that the tube rapidly became choked with carbon; the tar was strongly unsaturated and contained but little benzene. Aluminium, mercury, lead, zinc, and tungsten had little action. With copper a brown deposit rapidly formed, which soon choked the tube completely, whilst an unpleasant smelling tar was formed in small amount. Brass filings, on the other hand, only became slowly coated with carbon and gave a tar similar to that obtained with glass. Molten phenanthrene or anthracene did not react with acetylene in the presence or absence of aluminium chloride.

H. W.

The Interaction of Acetylene and Mercuric Chloride.

DAVID LEONARD CHAPMAN and WILLIAM JOB JENKINS (T., 1919, 115, 847—849).

Action of Methyl Sulphate on the Alkali and Alkali-earth Sulphates. J. GUYOT and L. J. SIMON (*Compt. rend.*, 1919, 168, 1204—1206. Compare this vol., i, 308).—The alkali and alkali earth sulphates if heated with methyl sulphate in sealed tubes at varying temperatures yield the pyrosulphate of the metal and dimethyl ether. This is shown to be due to the direct interaction of the two sulphates, and not to the intermediate formation of a sulphate such as sodium methyl sulphate, which would subsequently break down to the pyrosulphate and methyl ether. W. G.

The Hydrolysis of Ethyl Sulphite. A. BAGGESGAARD-RASMUSSEN (*Ber.*, 1919, 52, [B], 1069—1078).—The work of previous investigators has shown definitely that ethanesulphonate is formed in small amount during the hydrolysis of ethyl sulphite by alkali hydroxide, but an explanation of the phenomenon has not been given. The author has performed a series of quantitative experiments under different conditions, and has measured both the amount of base unused and the quantity of sulphite formed; the extent of hydrolysis as indicated by the first method is invariably slightly greater than that shown by the second, but a part of the difference is to be ascribed to an unavoidable slight oxidation of the sulphite. The actual formation of sodium ethanesulphonate is, however, placed beyond doubt. The author finds that the hydrolysis of ethyl sulphite by bases is in the main an absolutely

normal process; if, however, the action occurs slowly (as with the equivalent amount of alkali), small quantities (about 4—5%) of ethanesulphonate are produced. This compound is shown to be formed by the action of ethyl sulphite on the alkali sulphite first produced.

H. W.

Biochemical Formation of Mercaptans. F. F. NORD (*Ber.*, 1919, 52, [B], 1207—1211).—Neuberg and Nord (A., 1914, i, 1046) have shown that thioacetaldehyde is reduced to ethyl mercaptan by living yeast and also by zymase solution. The present investigation deals with the possibility of a similar process occurring with higher thioaldehydes. For biochemical purposes, it is unnecessary to isolate the difficultly accessible thioaldehydes in a state of purity; it is sufficient to treat the aldehydes with an alcoholic solution of ammonia and hydrogen sulphide, when homologues of thialdine are produced which behave as if they were mixtures of thioaldehyde and aldehydeimine, and possess the further advantage of being freely soluble in aqueous alcohol. *n*-Butaldehyde was treated in this manner and the product added to a solution of sugar in water which was undergoing brisk fermentation by yeast. Hydrogen sulphide was freely evolved, and, after fermentation had ceased, the liquor was found to contain *n*-butyl mercaptan, b. p. 95—102°, in small amount, together with indefinite compounds of higher boiling point. The presence of acetaldehyde was also established. In a similar manner, *iso*amyl mercaptan, b. p. 115—119°, was obtained from *iso*valeraldehyde; the thiovaleridine had a marked inhibitive action on the fermentation.

H. W.

Interaction of Mercuric and Cupric Chlorides Respectively and the Mercaptans and Potential Mercaptans. PRAFULLA CHANDRA RAY (T., 1919, 115, 871—878).

Water of Crystallisation: Compounds with $2\text{H}_2\text{O}$ and $3\text{H}_2\text{O}$. I. GUARESCHI (*Gazzetta*, 1919, 49, i, 134—140. Compare A., 1915, ii, 774).—Strontium formate loses its $2\text{H}_2\text{O}$ either (1) at 30°, or (2) at the ordinary temperature and a pressure of 20 mm. and in presence of sulphuric acid, the last $\frac{1}{2}\text{H}_2\text{O}$ being given up only very slowly; the anhydrous salt does not recover the water of crystallisation in the air. Zinc formate ($+2\text{H}_2\text{O}$) loses its water at 70° (not at 60°), the anhydrous salt reabsorbing about $1\frac{1}{2}\text{H}_2\text{O}$ from the air. Manganese formate loses its $2\text{H}_2\text{O}$ only at 70°, the last $\frac{1}{2}\text{H}_2\text{O}$ very gradually. Calcium chlorate ($+2\text{H}_2\text{O}$) undergoes complete dehydration at 50°, the anhydrous salt recovering all its water and then deliquescing in the air. Potassium ferrocyanide ($+3\text{H}_2\text{O}$) loses its water of crystallisation entirely either (1) at 50°, or (2) at 42° in a current of air, or (3) at the ordinary temperature in a desiccator over calcium chloride; in all cases, the last $\frac{1}{2}\text{H}_2\text{O}$ is released extremely slowly.

From the observation that many salts appear to yield their water

of crystallisation in definite fractions, the conclusion is drawn that the true molecular weights for the hydrated salts are multiples of those corresponding with the simplest empirical formulæ.

T. H. P.

The Solubility of Silver Acetate in Acetic Acid and of Silver Propionate in Propionic Acid. JOSEPH KNOX and HELEN REID WILL (T., 1919, 115, 853—854).

Stearic and Palmitic Esters of the Isomeric Propylene Glycols. L. ISABEL HOWE (*Trans. Roy. Soc. Canada*, 1918, [iii], 12, III, 13—18. Compare Ruttan and Roebuck, A., 1916, i, 115).—The 1:2- and 1:3-dihydroxypropanes may be directly esterified at high temperatures if constantly stirred, the optimum temperature of esterification varying with the acid used. After fusion, the mixture is freed from glycol by washing with hot water and from free acid by means of sodium hydrogen carbonate. The mono- and di-acid esters are separated by means of their different solubilities in alcohol. The following esters are described:

Propylene monostearate, $\text{OH}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{C}_{18}\text{H}_{35}\text{O}_2$, had m. p. $59\cdot5^\circ$, n^{60} 1·4424. The *distearate*, m. p. $72\cdot3^\circ$, crystallised in large, flaky crystals, n^{75} 1·4366.

Trimethylene monostearate, $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}_{18}\text{H}_{35}\text{O}_2$, had m. p. $60\cdot5^\circ$, n^{60} 1·4437, and the *distearate*, m. p. $64\cdot7^\circ$, n^{75} 1·4397.

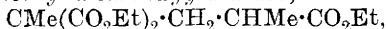
Propylene monopalmitate had m. p. $54\cdot2^\circ$, n^{60} 1·4405, and the *dipalmitate*, m. p. $68\cdot8^\circ$, n^{75} 1·4364.

Trimethylene dipalmitate had m. p. $56\cdot2^\circ$, n^{75} 1·4374. The monopalmitate was not isolated.

W. G.

The Optically Active $\alpha\alpha'$ -Dimethylglutaric Acids. ELOF MÖLLER (*Lunds. Univ. Årsskr.*, 1919, 15, 56 pp.; from *Chem. Zentr.*, 1919, i, 606—608).—The author gives two tables of the known optically active dibasic acids with two similarly placed asymmetric carbon atoms, and points out the relationship between melting point and optical activity. There appears to be no connexion between the difference of melting point of the isomerides and the magnitude of the specific rotation. *r- $\alpha\gamma$* -Dimethylglutaric acid has previously been resolved by means of the strychnine hydrogen salt, but the *l*-isomeride was not obtained pure (A., 1911, i, 12); the two antipodes have now been isolated in a state of purity, fission being effected with brucine or the α -phenylethylamines.

Ethyl r- $\alpha\gamma$ -dimethyl- α -carboxyglutarate,



b. p. $156\text{—}158^\circ/15\text{ mm.}$, is prepared by the action of ethyl β -bromoisobutyrate on ethyl sodiomalonate; when hydrolysed with sodium hydroxide, it yields *r- $\alpha\gamma$ -dimethyl- α -carboxyglutaric acid* as a sticky mass of indefinite m. p. The saturated aqueous solution contains 159 grams per litre at 20° . The dissociation constant, $100k=0\cdot220$. The *potassium dihydrogen* salt forms long crystals,

the *dipotassium* salt cannot be prepared, whilst the *normal potassium* salt forms small, transparent crystals (+ H_2O). Resolution of the acid could not be effected with α -phenylethylamine, quinine, or cinchonine, but was accomplished through the strychnine dihydrogen salts (the salt of the *d*-acid crystallises in colourless, anhydrous needles, that of the *l*-acid in prisms, + $4\text{H}_2\text{O}$). The active acids have m. p. 144—148°, $[\alpha]_D^{20} + 16.3^\circ$ and -15.6° in aqueous solution, and are more soluble in water than the racemic form.

r- α -Dimethylglutaric acid was partly resolved by strychnine and almost completely by brucine and the α -phenylethylamines, but not by cinchonine, cinchonidine, morphine, or quinine. With molar quantities of strychnine or brucine and *r*-acid, the salts of the *d*-acid separate first. Strychnine *d*- α -dimethylglutarate forms thin, transparent crystals (+ $2\text{H}_2\text{O}$), solubility 2.4 grams in 100 grams water; the corresponding salt of the *l*-acid forms colourless threads, readily soluble in water. The brucine salt of the *d*-acid (+ $2\text{H}_2\text{O}$) crystallises in colourless needles, 0.8 gram of which dissolves in 100 grams of water, whilst the salt of the *l*-acid forms transparent prisms, solubility 1.8 in 100. *l*-Phenylethylamine *d*- α -dimethylglutarate and *d*-phenylethylamine *l*- α -dimethylglutarate crystallise in needles, m. p. 157—158°, solubility 9 grams in 100 grams water; *d*-phenylethylamine *d*- α -dimethylglutarate and *l*-phenylethylamine *l*- α -dimethylglutarate have m. p. 144—145°, solubility 25 in 100. The strychnine salt of the *meso*-acid (+ $2\text{H}_2\text{O}$) forms threads, solubility 12 in 100, whilst the brucine salt dissolves to the extent of 18 parts in 100. *d*- and *l*-Phenylethylamine *meso*- α -dimethylglutarate dissolve freely in water. *d*- and *l*- α -Dimethylglutaric acids crystallise in needles or prisms, $[\alpha]_D^{20} + 39.8^\circ$ in aqueous solution. Examination of the barium hydrogen salt shows that the univalent ion has the same sign of rotation as the parent acid, whilst the bivalent ion of the normal salt is optically inactive. The *l*-anhydride, obtained by the action of acetyl chloride on the *d*-acid at 50—60°, forms cubic crystals, m. p. 41.5—42.5°, $[\alpha]_D^{18} - 69.6^\circ$ in benzene solution, whilst the *d*-anhydride crystallises in slender needles, m. p. 42—43.5°, $[\alpha]_D^{19} + 69.9^\circ$ in benzene solution. The *r*-anhydride, prepared by admixture of its components (the *r*-acid is only attacked by acetyl chloride with difficulty), has m. p. 33—34°.

The product obtained by the elimination of carbon dioxide from optically active α -dimethyl- α -carboxyglutaric acid consists of a mixture of about 40% active and 60% *meso*-dimethylglutaric acid; since the sign of rotation is the same as that of the carboxy-acid, it follows that the tri- and di-basic acids which rotate in the same direction are configuratively related.

H. W.

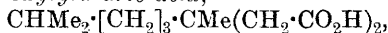
New $\beta\beta$ -Dialkylglutaric Acids. I. GUARESCHI (*Gazzetta*, 1919, 49, i, 124—133. Compare A., 1901, i, 630).—The following further acids have been prepared by the method formerly used;

ββ-Di-n-propylglutaric acid, $\text{CPr}^2(\text{CH}_2\cdot\text{CO}_2\text{H})_2$, prepared from $\alpha\gamma$ -dicyano- $\beta\beta$ -dipropylglutarimide, forms white crystals, m. p. 112—113°, and completely volatilises at a higher temperature, its vapour provoking coughing. The ammonium salt is highly soluble in water, its aqueous solutions giving precipitates of various colours with salts of heavy metals.

β-Ethyl-β-propylglutaric acid, $\text{CEtPr}(\text{CH}_2\cdot\text{CO}_2\text{H})_2$, crystallises in colourless, flattened needles or long laminæ, m. p. 71—72°, and has an intensely acid reaction.

β-Methyl-β-isobutylglutaric acid, $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CMe}(\text{CH}_2\cdot\text{CO}_2\text{H})_2$, has m. p. 63—65°.

β-Methyl-β-isoheptylglutaric acid,



forms crystals, m. p. 62—63°; the silver and zinc salts were analysed.

β-Methyl-β-nonylglutaric acid, $\text{CH}_3\cdot[\text{CH}_2]_8\cdot\text{CMe}(\text{CH}_2\cdot\text{CO}_2\text{H})_2$, crystallises in broad, colourless laminæ, greasy to the feel, m. p. 46·5—47·5°.

β-Methyl-β-hexylglutaric acid, $\text{C}_6\text{H}_{13}\cdot\text{CMe}(\text{CH}_2\cdot\text{CO}_2\text{H})_2$, forms crystals, m. p. 52—53°.

T. H. P.

Manganous Tartrate and Potassium Manganous Tartrate.

LEONARD DOBBIN (*J. Amer. Chem. Soc.*, 1919, **41**, 934—940).—Manganous tartrate is prepared by adding an equimolecular solution of sodium or potassium tartrate to either manganous sulphate or chloride solutions, when, on keeping, small, rose-tinted crystals separate. The crystals are monoclinic with axial ratios [$a:b:c=0\cdot816:1\cdot0\cdot699$, $\beta=100^\circ14'$]. It loses 14% of its water at 100°, and continues to lose water up to 180°, and at 200° darkens with slight decomposition. The crystals have the formula $\text{MnC}_4\text{H}_4\text{O}_6\cdot2\text{H}_2\text{O}$. All attempts by the author to prepare manganous potassium tartrate failed, hence it appears unlikely that this compound exists.

J. F. S.

New Explosive Substance Derived from Formaldehyde.

ANNIBALE MORESCHI (*Atti R. Accad. Lincei*, 1919, [v], **28**, i, 277—280).—The action of dry gaseous hydrogen chloride in the cold on commercial formaldehyde solution (about 40%) in a reflux apparatus yields, first, the compound, $\text{OH}\cdot\text{CH}_2\text{Cl}$. If the action is prolonged, a heavy liquid separates having a composition corresponding with the formula $\text{O}(\text{CH}_2\text{Cl})_2$. Treatment of this liquid at about 5° with a mixture of concentrated nitric and sulphuric acids results in liberation of hydrogen chloride, carbonyl chloride, and probably an oxygenated chlorine acid, and in separation of a colourless oil, D⁴ 1·52206, which, from its composition and its cryoscopic behaviour in benzene, appears to have the formula $\text{C}_2\text{H}_4\text{O}_6\text{N}_2$. This compound is extremely sensitive to shock, decomposing with detonation. Of the two possible constitutions, $\text{NO}\cdot\text{O}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{O}\cdot\text{NO}$, and $\text{NO}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{O}\cdot\text{NO}_2$, the latter is the more probable, since hydrolysis leads to the formation of formic

acid and nitromethane. The compound dissolves considerable proportions of cellulose nitrate even at 0° , and an explosive jelly containing 7% of cellulose nitrate (12.11% N) gives a greater increase in volume on explosion than one containing 7% of glyceryl nitrate.

T. H. P.

γ -Hydroxyvaleraldehyde. BURCKHARDT HELFERICH (*Ber.*, 1919, **52**, [B], 1123—1131).—Although α - and β -hydroxy-aldehydes of simple structure have been closely examined, the corresponding γ -derivatives do not appear to have been isolated, although their chemistry is exceptionally important owing to their near relationship to the sugars. The present communication describes an effort to fill this gap.

A solution of methylheptenol in glacial acetic acid is ozonised, diluted with ether and a little water, and treated with zinc dust until the perozonide is reduced; on distillation, a 78% yield of *γ -hydroxyvaleraldehyde* is obtained. It is a moderately mobile liquid with an odour resembling that of turpentine, b. p. $63\text{--}65^{\circ}/10$ mm., D_4^{20} 1.0167, n_D^{20} 1.4359, which mixes with water and organic solvents, but is salted out from its aqueous solution by potassium carbonate, but not by sodium sulphate or chloride. The freshly prepared solution contains the aldehyde in the unimolecular form. The *oxime*, *phenylhydrazone*, and *p-nitrophenylhydrazone* could only be obtained as oils, but the *p-bromophenylhydrazone* forms pale brown crystals, m. p. $88\text{--}89^{\circ}$ (corr.), after softening at about 85° , and *diphenylmethanedimethyldihydrazone* consists of colourless crystals, m. p. $84\text{--}85^{\circ}$ (corr.), after slight softening from 80° . The aldehyde yields a *bisulphite* compound, which is readily soluble in water. It does not reduce Fehling's solution in the cold and with only moderate rapidity on heating; ammoniacal silver solution is reduced in the cold. It is converted by concentrated aqueous sodium hydroxide into a crystalline mass, which is transformed into a dark terpinaceous oil when heated. Concentrated hydrochloric acid resinifies the aldehyde slowly in the cold, rapidly when warmed. Treatment of the aldehyde with 1% methyl-alcoholic hydrochloric acid at the ordinary temperature converts it into 5-methoxy-2-

methyltetrahydrofuran, $\begin{matrix} \text{CH}_2\text{---CHMe} \\ | \\ \text{CH}_2\text{---CH(OMe)} \end{matrix} > \text{O}$, a mobile, volatile liquid,

b. p. $116\text{--}118^{\circ}$ (corr.)/755 mm., D_4^{20} 0.9291, n_D^{20} 1.4110, which does not reduce boiling Fehling's solution and only reacts slowly with boiling ammoniacal silver solution. It is stable towards hot alkali and only slowly hydrolysed by hot acid. It does not appear to be hydrolysed by emulsin. When boiled with acetic anhydride, the aldehyde gives 5-acetoxy-2-methyltetrahydrofuran, mobile liquid, b. p. $73\text{--}78^{\circ}/9$ mm., D_4^{20} 1.037, n_D^{20} 1.4278, which is gradually converted by water at the ordinary temperature into acetic acid and the aldehyde.

H. W.

Preparation of Xylose from Maize Cobs. K. P. MONROE (*J. Amer. Chem. Soc.*, 1919, **41**, 1002—1003).—The method

described by La Forge and Hudson (*J. Ind. Eng. Chem.*, 1918, **10**, 925) is modified by removing the gum by digestion of the broken maize cobs with sodium hydroxide solution (1%) at 100° for one and a-half hours instead of performing the operation in an autoclave at 160°; the residue is hydrolysed by dilute sulphuric acid (4%), and the latter is subsequently removed with barium carbonate. The sugar solution thus obtained is less coloured than that prepared by previous methods, and crystallisation of the xylose takes place with uniform readiness. The yield is 8—10%. [See also, *J. Soc. Chem. Ind.*, 1919, August.] H. W.

New Sugar Isolated from a Sea-weed. EIJI TAKAHASHI (*J. Tokyo Chem. Soc.*, 1919, **40**, 157—166).—The author has isolated a new sugar from the hydrolytic product of the mucilaginous substance formed by boiling seaweed in water. The sugar crystallises from water in rectangular form, thicker in the middle, is exceedingly sweet, is soluble in alcohol, and has m. p. 152—153° and $[\alpha]_D^{20} + 80.75^\circ$. The molecular weight by the cryoscopic method is 179.3. Tests with resorcinol, phloroglucinol, Tollen's and Oshima's reagents show that it is not a ketose, pentose, or methyl-pentose. It yields lævulic acid, identified as the silver salt, and is thus shown to be a hexose. It strongly reduces Fehling's solution, is fermented by yeast, but not so readily as dextrose, and forms a *hydrazone* in the cold, m. p. 158—160°, which is soluble in methyl and ethyl alcohols and in hot water. The needle-shaped *osazone*, m. p. 193°, is soluble in the two alcohols, but not in water. The *phenylmethylhydrazone*, rectangular plates, has m. p. 191°, and the *p-bromophenylhydrazone*, m. p. 171—172°. Sodium amalgam reduces it to a hexahydric *alcohol*, prisms, m. p. 186—187°. The new sugar is very similar to galactose in specific rotatory power and in the m. p. of the corresponding alcohol, but differs in crystalline form, in failure to yield mucic and saccharic acids by oxidation with nitric acid, and in the m. p.'s of the various hydrazones and in the solubility of the *osazone* in methyl alcohol. From these analyses the author believes the new sugar to be an aldohexose, and names it *floridose*, and its alcohol, *floriditol*. This name is given because the sugar was first isolated from the red sea-weed *Florideae*. Sugars isolated from various sea-weeds, including *Chondrus elatus* Holms, *Ahnfeltia plicata*, and *Iridaea laminarioides* var. *ornucopiae*, are all easily crystallisable and are found to be absolutely identical with floridose. CHEMICAL ABSTRACTS.

The Preparation of Rhamnose. E. P. CLARK (*J. Biol. Chem.*, 1919, **38**, 255—256).—Liquid quercitron extract is hydrolysed by gently boiling with 3% sulphuric acid for half an hour. After removal of the sulphuric acid as barium sulphate, the material is concentrated to a thin syrup and eight volumes of 95% alcohol are slowly added with constant stirring. The filtrate from this precipitation is evaporated to a thick syrup under diminished pressure and the residue is dissolved in 95% alcohol. On the addition of $2\frac{1}{2}$ volumes of ether, a gummy substance is precipitated.

which is redissolved in alcohol and again precipitated by ether. From the extracts, on removal of the ether and concentration, rhamnose may be crystallised out. The yield is 50—51 grams of white rhamnose from 2 kilos. of the commercial quercitron extract.

J. C. D.

The Constitution of the Disaccharides. Part III. Maltose.

WALTER NORMAN HAWORTH and GRACE CUMMING LEITCH (T., 1919, 115, 809—817).

Improvements Relating to the Preparation of Amines.

WILLIAM RINTOUL, JOHN THOMAS, and NOBEL'S EXPLOSIVES Co., LTD. (Brit. Pat., 127740).—Tertiary amines are separated from admixture with primary and secondary amines by converting the latter into the corresponding urethanes by treatment with ethyl chloroformate in the cold in presence of aqueous sodium carbonate. The unchanged tertiary base is removed from the residual, oily product by washing with dilute mineral acid, and is recovered by treatment of the acid washings with alkali, whilst the primary and secondary bases are regenerated by the hydrolysis of the urethanes. [See, further, *J. Soc. Chem. Ind.*, 1919, August.]

G. F. M.

Polypeptides containing Glutamine and the Question of the Occurrence in Proteins.

H. THIERFELDER and E. VON CRAMM [with ALFRED WALTHER] (*Zeitsch. physiol. Chem.*, 1919, 105, 58—82).—It has been suggested that glutamine and asparagine are components of protein rather than glutamic and aspartic acids (Osborne and Gilbert, A., 1906, i, 324; Osborne, Leavenworth, and Braunleht, A., 1909, i, 72).

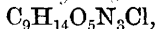
A study of the formation of ammonia during the acid hydrolysis of gliadin, polypeptides containing glutamine, and glutamine itself leads the authors to support the view that glutamine is a component of the protein molecule.

The preparation of four dipeptides and of one tripeptide containing glutamine is described.

Chloroacetyl-d-glutamine, $C_7H_{11}O_4N_2Cl$, fine needles from ethyl acetate, m. p. 130—132°, $[\alpha]_D^{16} = -10.33$ to -10.45° .

Glycyl-d-glutamine, $C_7H_{13}O_4N_3$, crystallises with one molecule of water, and decomposes at 199—200°, $[\alpha]_D^{19} = -2.47^\circ$. This dipeptide has an acid reaction. It is precipitated by phosphotungstic acid, but is soluble in excess, and gives no biuret test.

Chloroacetyl-d-glutaminyglycine ethyl ester, $C_{11}H_{18}O_5N_3Cl$, needles, m. p. 198°. *Chloroacetyl-d-glutaminyglycine*,



needles, m. p. 162—163°. *Glycyl-d-glutaminyglycine*, $C_9H_{16}O_5N_4$, needles, decomposes at 201°, $[\alpha]_D^{19} = -28.4^\circ$. This tripeptide possesses an acid reaction, and is precipitated by phosphotungstic acid, but the precipitate is soluble in an excess of the reagent. It is not precipitated by mercuric chloride, tannic acid, phosphomolybdic acid, basic lead acetate, or saturated ammonium sulphate solution. It gives a bluish-violet biuret reaction.

d- α -Bromopropionyl-d-glutamine, $C_8H_{13}O_4N_2Br$, m. p. 156—157°, $[\alpha]_D^{19} = +9.03-9.3^\circ$. **d-Alanyl-d-glutamine**, $C_8H_{15}O_4N_3$, prisms, m. p. 222° (decomp.), $[\alpha]_D^{18} = -9.2^\circ$. It possesses an acid reaction to litmus and gives no biuret test.

l- α -Bromopropionyl-d-glutamine, $C_8H_{13}O_4N_2Br$, rosettes of needles, m. p. 132°. When recrystallised from ethyl acetate the substance gave a rotation in methyl alcohol of $[\alpha]_D^{19} = -17.42^\circ$. The substance, recrystallised from water, gave in the same concentration $[\alpha]_D = -16.4^\circ$. No explanation is put forward. **l-Alanyl-d-glutamine**, $C_8H_{15}O_4N_3$, needles, m. p. 212—213°, $[\alpha]_D^{18} = -20.1^\circ$. This substance is acid to litmus and gives no biuret reaction.

d- α -Bromoisohexoyl-d-glutamine, $C_{11}H_{19}O_4N_2Br$, m. p. 150°, $[\alpha]_D^{19} = +20.8^\circ$, $[\alpha]_D^{20} = +20.55^\circ$, crystallises in prisms. **l-Leucyl-d-glutamine**, $C_{11}H_{21}O_4N_3$, needles, m. p. 235—236°, $[\alpha]_D^{18} = +12.6^\circ$. It is acid to litmus and gives no biuret reaction. J. C. D.

Catalytic Action of Hydrogen Peroxide on Potassium Ferro- and Ferri-cyanides. E. LÜCK (*Apoth. Zeit.*, 1919, **34**, 87; from *Chem. Zentr.*, 1919, i, 610—611).—If an aqueous solution of potassium ferricyanide is warmed for about two minutes at 45° with 10% of hydrogen peroxide and allowed to cool, almost black *crystals*, $2K_3FeC_6N_6 \cdot 3H_2O_2$, are obtained which are very sparingly soluble in water, mol. wt. 759.82. In a similar manner, potassium ferrocyanide gives the *compound*, $2K_4FeC_6N_6 \cdot 3H_2O_2$. H. W.

Modified Graphic Formulæ for Organic Cyclic Compounds.

ALEXANDER LOWY (*J. Amer. Chem. Soc.*, 1919, **41**, 1029—1030).—The author recommends the advisability of indicating the double bonds in cyclic compounds by heavy lines and the single bonds by light lines. A series of typical examples is given.

H. W.

Freezing-point Curves of Mixtures of Nitro- and Dinitrobenzene.

K. LEHMSTEDT (*Zeitsch. ges. Schiess. u. Sprengstoffw.*, 1918, **13**, 118—119; from *Chem. Zentr.*, 1919, i, 708).—The author has determined the freezing point of various solutions of pure *m*-dinitrobenzene and of a mixture of *o*-, *m*-, and *p*-dinitrobenzene (6.5%, 92.0%, and 1.5% respectively) in nitrobenzene. The composition of nitrated products can be readily elucidated from the freezing-point curve for the pure dinitrobenzene and for the technical mixture of isomerides. The curve has two eutectic points, probably due to the fact that solutions which contain little dinitrobenzene are not caused to crystallise by seeding with dinitrobenzene. H. W.

The Reduction of 2 : 3-, 3 : 4-, and 2 : 5-Dinitrotoluenes.

JAKOB MEISENHEIMER and ERICH HESSE (*Ber.*, 1919, **52**, [B], 1161—1177).—Some years ago (A., 1904, i, 150; 1906, i, 642) it was shown that *o*- and *p*-dinitrobenzenes are converted by cautious reduction in alkaline solution into dark-coloured salts of *diaci*-dinitrocyclohexadienes, which, when acidified, rapidly pass into

nitronitrosobenzenes. The experiments with *o*-dinitrobenzene have been repeated on a large scale, the products now obtained being *o*-nitronitrosobenzene (19% of that theoretically possible), nitrobenzene (31%), *o*-nitrophenol (14%), a little *o*-nitroaniline, and resinous matter.

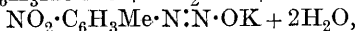
The work has also been extended to 2:3-, 3:4-, and 2:5-dinitrotoluenes, which are found to behave in a precisely similar manner.

3:4-Dinitrotoluene, m. p. 59—60°, is conveniently prepared by oxidising 3-nitro-*p*-toluidine by means of Caro's acid to 3-nitro-4-nitrosotoluene, and completing the oxidation of the latter with nitric acid. Reduction of 3:4-dinitrotoluene by hydroxylamine is effected in the usual manner, but the salt which is produced cannot be isolated on account of its ready solubility. On acidification, the following substances are obtained: 3-nitro-4-nitrosotoluene, m. p. 143°; 4-nitro-3-nitrosotoluene, yellow leaflets, m. p. 141°; a mixture of *m*- and *p*-nitrotoluenes, *p*-nitro-*m*-cresol, m. p. 56°, and resinous products, from which nothing definite could be isolated. Potassium diaci-3:4-dinitromethyl- $\Delta^{1,5}$ -cyclohexadiene is prepared by the addition of an ethereal solution of potassium ethoxide to a suspension of 3-nitro-4-nitrosotoluene in ether, and forms an amorphous powder of dark red colour which is extraordinarily sensitive to moisture; when treated with aqueous acid, it yields a mixture of nitronitrosotoluenes.

2:3-Dinitrotoluene, m. p. 96—97°, is best obtained by the nitration of acet-*o*-toluide by nitric acid in the presence of acetic acid, and decomposition of the mixture of 3- and 5-nitroacet-*o*-toluides with hydrochloric acid; the separation of the isomeric amines is accomplished by diluting the acid solution largely with water, when the very feebly basic 3-nitro-*o*-toluidine is precipitated; the latter is converted by Caro's acid into 3-nitro-2-nitrosotoluene, pale yellow leaflets, m. p. 126—127° (decomp.), which is transformed by nitric acid into 2:3-dinitrotoluene. (6-Nitro-2:4'-dimethylazobenzene, red prisms, m. p. 65·5—66°, is obtained by condensing 3-nitro-2-nitrosotoluene with *p*-toluidine in glacial acetic acid solution; if aniline is used, 6-nitro-2-methylazobenzene is obtained as a red oil, b. p. 215°/11 mm., which does not solidify after many months.) Reduction of 2:3-dinitrotoluene with hydroxylamine follows the normal course, yielding 2-nitro-3-nitrosotoluene, yellow leaflets, m. p. 92—93°, a mixture of *o*- and *m*-nitrotoluenes, and 3-nitro-*o*-cresol, m. p. 69—70°. The potassium salt of diaci-2:3-dinitromethyl- $\Delta^{4,6}$ -cyclohexadiene is prepared from 3-nitro-2-nitrosotoluene, and is very sensitive to moisture.

5-Nitro-2-nitrosotoluene, almost colourless crystals, m. p. 143—144°, is obtained by the action of Caro's acid on the corresponding amine (it condenses with aniline to yield 4-nitro-2-methylazobenzene, red prisms, m. p. 98—99°), and is readily transformed into 2:5-dinitrotoluene, m. p. 50—51°. The latter is reduced by hydroxylamine, and the solution yields on acidification 5-nitro-2-nitrosotoluene and dinitroazoxytoluene, dark brown prisms, m. p. 188—189°. The potassium salt of diaci-2:5-dinitro-

methyl-Δ³⁻⁶-cyclohexadiene is obtained as with the other isomerides, and forms an unstable, red salt, which, when acidified, gives dinitroazoxytoluene. When reduction of 2:5-dinitrotoluene by hydroxylamine is effected in highly concentrated solution, *potassium nitrotolueneisodiazotate*, $C_7H_6O_3N_3K \cdot H_2O$, is precipitated in yellow needles, m. p. 202° (decomp.); the substance owes its origin to the action of hydroxylamine on the intermediately formed nitroso-derivative, $NO_2 \cdot C_6H_3Me \cdot NO + NH_2 \cdot OH + KOH =$



as is shown by its formation by the interaction of hydroxylamine with 5-nitro-2-nitrosotoluene. Attempts are also described to prepare it by the diazotisation of 5-nitro-*o*-toluidine and treatment of the product with sodium hydroxide solution, but the yellow, crystalline material exploded with great violence. H. W.

Preparation of Liquid Hydrocarbons by the Action of Aluminium Chloride on Naphthalene under Pressure.

FRANZ FISCHER (*Ges. Abhand. Kennt. Kohle*, 1917, 1, 237—244; from *Chem. Zentr.*, 1917, ii, 584).—[With WILHELM SCHNEIDER.]—A mixture of naphthalene (100 grams) and powdered aluminium chloride (4 grams), when boiled under reflux during three hours and subsequently distilled, yielded about 47 grams of naphthalene impregnated with oil and a residue of 47 grams of a brittle pitch which, when heated to redness, gave a small amount of viscous distillate and much coke. On the other hand, when naphthalene (250 grams) and aluminium chloride (10 grams) were heated under pressure (up to ten atmospheres) at 330° during twenty minutes, 124.5 grams of oil containing naphthalene and 108 grams of charred matter were obtained, from which 92 grams of non-solidifying oil were isolated by freezing and pressing. It is therefore possible to convert technically pure naphthalene by 4% of aluminium chloride in autoclaves into a mixture of liquid hydrocarbons, the yield of which is 40%; the remainder of the naphthalene is converted into a mixture of pitch and carbon, since a portion of the naphthalene is hydrogenated at the expense of the other portion.

[With SIEGFRIED HILPERT.]—1055 Grams of non-solidifying oil were obtained from 3250 grams of naphthalene and 130 grams of aluminium chloride; after treatment with calcium oxide to remove hydrogen chloride, the oil was distilled, and yielded 4% b. p. below 150° , 79% b. p. 150 — 300° , and 16% residue of higher b. p. The chief fraction, when cooled to 0° , deposited 27% of its weight of naphthalene, so that the remainder, which had b. p. 150 — 300° and did not solidify at 0° , constituted 57% of the total oil, or 18% of the original naphthalene. The middle fraction contained 8.4% of hydrogen and 91.5% of carbon. Its heat of combustion was 9332 Cal. (naphthalene, 9628 Cal.; dihydronaphthalene, 10,092 Cal.). The viscosity in Engler's apparatus was 1.16 at 20° and the flash point 70° (Pensky Martens), 75° (open test). The hydrogenated naphthalene could not be burnt in ordinary petroleum lamps without formation of soot. H. W.

Preparation of Thickening Material for Lubricating Oils from Naphthalene.

FRANZ FISCHER (*Ges. Abhand. Kennt. Kohle*, 1917, 1, 254; from *Chem. Zentr.*, 1919, ii, 584).—Complex compounds, formed by the condensing action of aluminium chloride, remain undecomposed when naphthalene and aluminium chloride are heated at a moderate temperature (compare preceding abstract). Thus, when crude naphthalene (500 grams) is heated in an autoclave with aluminium chloride (50 grams) (the maximum temperature and pressure being respectively 55° and two atmospheres) and the product is distilled with steam, a black, syrupy, viscous residue remains which, after being filtered through cloth while hot, gives with three parts of a fatty tar oil, a black lubricating oil of good quality.

H. W.

Conversion of Naphthalene into Liquid Products.

HERMANN NIGGEMANN (*Ges. Abhand. Kennt. Kohle*, 1917, 1, 255—258; from *Chem. Zentr.*, 1919, ii, 584—585. Compare preceding abstracts).—Attempts have been made to methylate naphthalene by heating it with polymethylbenzenes in the presence of aluminium chloride, since this substance not infrequently causes a wandering of the methyl groups in methylbenzenes. When xylene, b. p. 134—135°, was heated to boiling with aluminium chloride for three hours, a mobile, dark brown, and a viscous, black oil were obtained from the former, of which fractions boiling below and above xylene were isolated. Noticeable action did not occur when dry hydrogen chloride was passed through a suspension of dry aluminium hydroxide in xylene. Under similar conditions, solvent naphtha (25 grams, b. p. 150—175°) yielded fractions, b. p.'s 145—150° (2 grams), 150—175° (15 grams), 175—205° (3 grams), whilst the residue after decomposition with hydrochloric acid gave 2 grams, b. p. 150—280°. A mixture of naphthalene and xylene yielded an oil, b. p. 125—220°, which partly solidified, whilst a mixture of naphthalene and solvent naphtha gave small fractions, b. p.'s 110—150° and 150—175°, and a larger fraction, b. p. 175—225°, consisting of naphthalene impregnated with oil. When naphthalene was boiled with aluminium chloride (4%) during one and a-half hours, and the product treated with hot dilute hydrogen chloride and distilled, oily naphthalene was obtained at 210—225°, and a substance, which solidified to a yellow, waxy mass when the distillation was continued to 220° in an absolute vacuum.

Acenaphthene when boiled with aluminium chloride (4%) for one and a-half hours yielded a yellowish-green, fluorescent oil, b. p. 195—265°, which remained liquid at the ordinary temperature, but deposited acenaphthene at 0°. Similarly, anthracene gave an oil, b. p. 200—300°, which formed a mass of orange crystals at the ordinary temperature, whilst phenanthrene yielded a yellowish-green, fluorescent oil, which partly solidified at 0° and became liquid again at the ordinary temperature.

H. W.

Conversion of Naphthalene into Liquid Products by Alkylation. FRANZ FISCHER and WILHELM SCHNEIDER (*Ges. Abhand. Kennt. Kohle*, 1917, 1, 227—230; from *Chem. Zentr.*, 1919, ii, 585. Compare preceding abstracts).—The object of the investigation was the technical liquefaction of naphthalene by alkylation in the simplest possible manner. Naphthalene (5 grams) when heated with absolute alcohol (4.5 c.c.) and zinc chloride (10 grams) at 290—300° during thirty-six hours yielded 0.2 gram of recovered naphthalene and 5.1 grams of a reddish-brown oil with a green fluorescence. By treatment of crude naphthalene (100 grams) with alcohol (96%, 120 c.c.) and zinc chloride (200 grams regenerated, 200 grams fresh substance) at 180—190° during sixty hours it gave 112 grams of a dark brown oil with a green fluorescence which, on distillation, yielded a small fraction, b. p. below 240°, 98 grams of a volatile, yellow oil, b. p. 240—300°, and 12 grams of dark brown, viscous, residual oil; naphthalene did not separate from these oils when cooled with ice-water. The zinc chloride cannot be replaced by granulated calcium chloride, sulphuric acid, sodium hydrogen sulphate, or anhydrous magnesium chloride. When naphthalene (5 grams) was heated with methyl alcohol (3.3 c.c.) and zinc chloride (10 grams) at 290—300° during twelve hours, 3.8 grams of oil were obtained, together with 0.8 gram of naphthalene. A mixture of naphthalene and phenol when heated with zinc chloride at 290—300° gave a considerable amount of carbon and large amounts of unchanged substances. Acetone appeared to react with naphthalene in the presence of zinc chloride with elimination of water. Acetylene and ethylene did not react with naphthalene at 100—200° in the presence of aluminium chloride.

H. W.

Conversion of Naphthalene into Liquid Products by Hydrogenation in Pressure Furnaces in the Presence of Non-metallic Catalysts. FRANZ FISCHER and HERMANN NIGGEMANN (*Ges. Abhand. Kennt. Kohle*, 1917, 1, 231—236; from *Chem. Zentr.*, 1919, ii, 585—586).—The experiments were performed in an electrically heated, horizontal furnace capable of withstanding high pressures. Naphthalene was found to be very resistant to high temperatures, and, except for slight discoloration and traces of separation of carbon, remained unchanged when heated during one hour at 500° in the presence or absence of copper, iron, coke, or selenium; in the presence of 1% of iodine, it became intensely black, owing to separation of carbon. The best conditions for obtaining liquid products from naphthalene by hydrogenation consist in employing high temperatures and pressures. In the absence of catalysts or in the presence of selenium, the liquefaction is minimal. Iodine, on the other hand, is an active catalyst; naphthalene is completely liquefied by heating with 1% of iodine at 550° for one hour in an atmosphere of hydrogen (pressure to about 170 atmospheres) to an oil with a

blue fluorescence, a mirror of carbon being also formed. Carbonisation occurs more readily at high than at low pressures; separation of carbon at a hydrogen pressure less than 50 atmospheres does not occur below 800°, with 50 atmospheres at 800°, with 100 atmospheres at 550°, with 170 atmospheres below 550°. The hydrogenated oils solidify more or less completely after a few days, probably owing to oxidation and separation of dissolved naphthalene. H. W.

Constitution of certain Polynitro-compounds. J. BISHOP TINGLE and WALTER ALBERT LAWRENCE (*Trans. Roy. Soc. Canada*, 1918, [iii], **12**, III, 7—11).—The authors have determined the constitution of the nitration products of picranilide and diphenylamine obtained by Tingle and Blanck (compare A., 1908, i, 778), and shown by Tingle and Burke to be tetranitrodiphenylamines (compare A., 1910, i, 21). By the action of nitric acid on picranilide in the presence of oxalic acid, the product obtained is 2:4:6:4'-tetranitrodiphenylamine, m. p. 216°. By the action of trichloroacetic and nitric acids, picranilide yields *s*-tetranitrodiphenylamine, m. p. 191°, together with some bis-2:4-tetranitrodiphenylamine, m. p. 179—180°. On nitrating diphenylamine itself, three compounds are obtained, namely, *s*-tetranitrodiphenylamine as the main product, together with a small quantity of a *tetranitrodiphenylamine*, m. p. above 250°, and a *compound*, not identified. W. G.

Salts of Hexanitrodiphenylamine. H. KAST and A. LANGHANS (*Zeitsch. ges. Schiess. u. Sprengstoffw.*, 1919, **14**, 1—4, 25—27; from *Chem. Zentr.*, 1919, i, 719).—The acidic character of hexanitrodiphenylamine, due to the presence of the imide-hydrogen atom, enables it to form soluble salts of orange-yellow to blood-red colour. Readiness of salt formation is considerably restricted by the sparing solubility of the parent substance. A series of salts has, however, been prepared by agitating and warming an aqueous or alcoholic solution or suspension of the requisite metallic oxides, hydroxides, or carbonates with hexanitrodiphenylamine. The *magnesium* salt is the most readily soluble, and may conveniently be used in obtaining the salts of the heavy metals by double decomposition. The salts, with the exception of those of magnesium and ammonium, are more sensitive than the parent substance. The lead salt is the most sensitive, followed in order by the copper, sodium, iron, potassium, calcium, and ammonium salts. The sequence, with the exception of the sodium salt, is therefore the same as with the salts of picric acid and trinitrocresol. H. W.

Preparation of Hexanitrodiphenylamine from Chlorobenzene. E. J. HOFFMAN and PERRY A. DAME (*J. Amer. Chem. Soc.*, 1919, **41**, 1013—1020).—The preparation is effected in the following stages; (i) nitration of chlorobenzene to chlorodinitro-

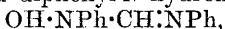
benzene by a mixture of nitric and sulphuric acids, (ii) formation of dinitrodiphenylamine by heating chlorodinitrobenzene with aniline, (iii) preparation of tetranitrodiphenylamine by the action of nitric acid on the dinitro-compound (compare Carter, *Zeitsch. ges. Schiess. Sprengs.*, 1913, **8**, 205, 251), and (iv) conversion of tetranitrodiphenylamine into hexanitrodiphenylamine by nitric-sulphuric acid, the latter procedure being a modification of Carter's method. The best experimental conditions for each stage are fully described, and the yield of hexanitro-derivative is 68.62% of that theoretically possible, calculated on the basis of chlorobenzene used. The authors' results lead them to the conclusion that the intermediate isolation of the tetranitro-compound is probably unnecessary, and that the dinitro- can be converted directly into the hexanitro-derivative. The latter crystallises in fine, yellow needles, m. p. 240—250° (decomp.). It is a very brisant explosive, scarcely suitable for explosive purposes except when mixed with other substances. It is much more poisonous than glyceryl nitrate, and causes severe blisters, resembling burns, when it comes in contact with the skin. The fine dust especially affects destructively the mucous membranes of the mouth, nose, and lungs. H. W.

Catalytic Hydrogenation of Schiff's Bases. ALPH. MAILHE (*Bull. Soc. chim.*, 1919, [iv], **25**, 321—325).—Schiff's bases, obtained by condensing an aldehyde with a primary amine, readily undergo hydrogenation when passed with hydrogen over reduced nickel at 200—230°, giving the corresponding secondary amine. At the same time, there is a slight secondary reaction, represented by the equation $R \cdot CH : NR' + 2H_2 = R \cdot CH_3 + R' \cdot NH_2$. Satisfactory yields were obtained in this manner from five of these bases. W. G.

N-Phenylhydroxylamine and Methyl Sulphate. EUG. BAMBERGER and ALEXANDER LANDAU (*Ber.*, 1919, **52**, [B], 1093—1110).—Since previous attempts to prepare alkyl derivatives of N-phenylhydroxylamine by means of methyl iodide, methyl bromide, or diazomethane did not give the desired result, the authors have examined the action of methyl sulphate without, however, being able to effect the isolation of the ethers.

The majority of the experiments were performed by adding methyl sulphate and sodium hydrogen carbonate to an aqueous solution or suspension of phenylhydroxylamine at 0°. In these circumstances the most readily isolable product is the methylenediphenylhydroxylamine, $CH_2(NPh \cdot OH)_2$, which had previously been obtained by the use of diazomethane as methylating agent (Bamberger and Tschirner, A., 1900, i, 342). In addition, small quantities of azoxybenzene, aniline, and mono- and di-methyl-anilines were isolated, but it is uncertain whether the latter were produced by the methylation of aniline or by the decomposition of phenylmethylhydroxylamine. The methylene-diphenylhydroxylamine was accompanied by a second base which was without doubt formed from it during its purification, and which was identified as glyoxime-N-phenyl ether, $O : NPh : CH - CH : NPh : O$. Small amounts

of oily and crystalline substances were also produced, but in quantity scarcely sufficient for complete identification. Among these was a substance crystallising in colourless leaflets, m. p. about 132° (which closely resembled diphenyl-*N*-hydroxyformamidine,



but complete identity could not be established), a product, m. p. 232° , and an impure oil which possibly contained phenylmethylhydroxylamine. Since the total weight of these products did not correspond with the amount of material employed, the residual aqueous solution was treated with sulphuric acid and sodium nitrite, when *p*-nitrodimethylaniline, m. p. 162° , and *o*-nitrodimethylaniline were obtained. The only probable source of these substances was dimethylaniline *N*-oxide, which was actually isolated in the form of its picrate; it is remarkable that the amount of the latter generally appears to increase when the reaction mixture is preserved.

When phenylhydroxylamine and methyl sulphate were mixed, the reaction became extremely violent after a short time; in the presence of ether as diluent, the action could be conveniently regulated and the products were dimethylaniline oxide, methylenedi-phenylhydroxylamine, small quantities of aniline, and the methylanilines and substances of unknown composition. A portion of the phenylhydroxylamine was removed from action in the form of its methosulphate. In addition, a reddish-brown oil was obtained which possibly contains phenylhydroxylamine *O*-methyl ether.

Attempts were also made to use nascent phenylhydroxylamine by reducing nitrobenzene with zinc and ammonium chloride in the presence of methyl sulphate; the products, however, were the same as those obtained previously.

The production of methylenedi-phenylhydroxylamine during the methylation of phenylhydroxylamine is explained in the following manner: the primary product of the change is phenylmethylhydroxylamine, which spontaneously decomposes into formaldehyde and aniline, $\text{Ph}\cdot\text{NMe}\cdot\text{OH} = \text{CH}_2\text{O} + \text{PhNH}_2$; the formaldehyde then condenses with more phenylhydroxylamine to yield methylenedi-phenylhydroxylamine. The conversion of the latter by boiling water or alcohol into glyoxime-*N*-phenyl ether depends on its hydrolysis to formaldehyde and *N*-phenylhydroxylamine and reaction between these substances: $\text{OH}\cdot\text{NPh}\cdot\text{CH}_2\cdot\text{NPh}\cdot\text{OH} + \text{H}_2\text{O} = \text{CH}_2\text{O} + 2\text{NHPH}\cdot\text{OH}$ and $2\text{CH}_2\text{O} + 2\text{NHPH}\cdot\text{OH} = \text{O}\cdot\text{NPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{NPh}\cdot\text{O} + 2\text{H}_2\text{O} + \text{H}_2$. In an intermediate stage the formaldehyde condenses under the basic influence of phenylhydroxylamine to glycollaldehyde,

which reacts thus: $\text{OH}\cdot\text{CH}_2\cdot\text{CHO} \xrightarrow{\text{NHPH}\cdot\text{OH}} \text{OH}\cdot\text{NPh}\cdot\text{CH}_2\cdot\text{CHO}$ or $\text{OH}\cdot\text{NPh}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{NPh}\cdot\text{O} \rightarrow \text{O}\cdot\text{NPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{NPh}\cdot\text{O} + \text{H}_2$. The liberated hydrogen is used in the reduction of a further molecule of phenylhydroxylamine.

H. W.

Attempts to Prepare β -Phenylhydroxylamine *O*-Methyl Ether. EUG. BAMBERGER (*Ber.*, 1919, 52, [B], 1111—1123).—Attempts to prepare the substance by the action of methyl iodide or

methyl bromide under widely varied conditions did not lead to the desired result, the products generally consisting of azoxybenzene, azobenzene, aniline, and methylaniline. Similarly, the product could not be obtained by the hydrolysis of *N*-benzoylphenylhydroxylamine *O*-methyl ether or of phenyloxyurethane *O*-methyl ether. Apparently, phenylhydroxylamine *O*-methyl ether dissociates with extreme readiness under the influence of hydroxyl ions into $\text{PhN} <$ (or azobenzene) and methyl alcohol.

[With K. BLASKOPF and ALEXANDER LANDAU.]—*N*-Benzoylphenylhydroxylamine and dibenzoylphenylhydroxylamine are prepared by the action of benzoyl chloride on an aqueous solution of phenylhydroxylamine in the presence of sodium hydrogen carbonate or sodium acetate, and are conveniently separated by taking advantage of the solubility of the former and insolubility of the latter in aqueous ammonia; they form colourless needles, m. p. 121—122°, and shining needles, m. p. 117—118° respectively. *N*-Benzoylphenylhydroxylamine *O*-methyl ether, cubic crystals, m. p. 54·5—55°, is prepared by the action of methyl iodide and sodium methoxide on the mono-benzoyl compound or, more conveniently, by the methyl sulphate method. When hydrolysed with boiling methyl-alcoholic potassium hydroxide, it yields azobenzene; with aqueous alkali in the presence of acetone, it gives benzoic acid, azobenzene, aniline, and, possibly, *p*-anisidine; with aqueous alkali the chief products are benzoic acid and azobenzene. Benzoic acid, *p*-aminophenol, aniline, and *p*-anisidine are formed when sulphuric acid and methyl alcohol are used, whilst when the latter is replaced by ethyl alcohol *p*-phenetidine is produced.

[With F. TSCHIRNER.]—*Hydroxyphenylurethane*,
 $\text{NPh(OH)·CO}_2\text{Et}$,

colourless, silky prisms, m. p. 47·5°, is prepared by the action of ethyl chloroformate on an ethereal solution of phenylhydroxylamine (the sodium derivative forms fine, colourless crystals), and is reduced by zinc dust and acetic acid to phenylurethane, m. p. 51°. *m*-Tolylhydroxyurethane is similarly prepared and has m. p. 30°. When treated with methyl iodide and potassium methoxide, phenylhydroxyurethane is converted into *methoxyphenylurethane*, mobile oil, b. p. 124°/12 mm. The latter is hydrolysed by aqueous ammonia, yielding, as main products, ethylurethane and azobenzene.

H. W.

Preparation of Acyl Derivatives of a *p*-Aminophenyl Ether. GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 310967; from *Chem. Zentr.*, 1919, ii, 422—423).—*p*-Aminophenyl allyl ether is caused to react with aliphatic acids, acid anhydrides, or acid haloids if necessary in the presence of a suitable diluent or condensing agent. *p*-Acetylaminophenyl allyl ether, shining leaflets, m. p. 94°, is thus obtained by boiling the amino-ether with acetic anhydride. *Lactylaminophenyl allyl ether*, from the amino-ether and lactide at 150°, forms shining leaflets, m. p. 87°. *isoValeryl-p-aminophenyl allyl ether*, small needles, m. p. 95°, is obtained from the acid, whilst α -bromoisovaleryl-*p*-aminophenyl allyl ether, shining

leaflets, m. p. 131° , is prepared from the amino-ether and α -bromo-*isovaleryl* bromide in the presence of ether and sodium carbonate. The substances are powerful soporifics, which also possess sedative and antineuralgic properties. H. W.

***p*-Cymene. II. Utilisation of Cymene for the Preparation of Photographic Developers.** HERBERT A. LUBS (*J. Ind. Eng. Chem.*, 1919, **11**, 455—456. Compare Andrews, A., 1918, i, 339).—Cymene is nitrated and the nitro-derivative reduced to 4-*isopropyl-o*-toluidine (*ibid.*), which is converted through the diazo-reaction into carvacrol. This is transformed into the *p*-nitroso-compound by adding sodium nitrite to an alcoholic solution of the phenol, saturated with hydrogen chloride, and the product is dissolved in 10% ammonia solution and reduced by hydrogen sulphide, when *p*-aminocarvacrol [$\text{Me}:\text{Pr}:\text{OH}:\text{NH}_2=1:4:2:5$] is precipitated in colourless leaflets. This is a better developer than *p*-aminophenol and gives as good tones as metol, but it does not keep quite so well as this in the developing bath.

Thymoquinol may also be made from sulphonated carvacrol, but the yields are poor and it offers no advantages over quinol. *p*-Aminothymol is also not a suitable developer. J. C. W.

3-Nitro-*o*-toluic Acid. S. GABRIEL and ARTHUR THIEME (*Ber.*, 1919, **52**, [B], 1079—1092).—3-Nitro-*o*-toluic acid, the last of the ten theoretically possible nitrotoluic acids, has been recently described by Mayer (A., 1915, i, 958); the authors find that some of his data are incorrect, and have re-investigated the substance.

Acet-*o*-toluidide is converted by nitric acid in acetic acid solution in the presence of acetic anhydride into a mixture of 3- and 5-nitroacet-*o*-toluidides, which are hydrolysed with concentrated hydrochloric acid; under suitable conditions, 3-nitro-*o*-toluidine can be precipitated from this solution by addition of water, whilst the 5-nitroisomeride remains dissolved. The former is reduced by hydriodic acid to the corresponding diamine, m. p. $63\text{--}64^{\circ}$, the relative position of the amino-groups following from its transformation into 4(or 7)-methylbenziminazole, m. p. 145° (*hydrochloride*, rhombic plates which do not melt below 300°). 3-Nitro-*o*-toluonitrile, silvery leaflets, m. p. $109\text{--}110^{\circ}$, is prepared by Sandmeyer's method and treatment of the crude product with alcohol or with nitric acid; it is reduced by hydriodic acid and phosphorus to 3-amino-*o*-toluonitrile, m. p. $127\text{--}128^{\circ}$, which by further application of Sandmeyer's reaction gives 3-methylphthalonitrile, colourless needles, m. p. 143° , from which 3-methylphthalimide, m. p. $189\text{--}190^{\circ}$, is prepared by the action of sulphuric acid. Attempts to hydrolyse 3-nitro-*o*-toluonitrile directly to the acid were unsuccessful, but it is transformed by sulphuric acid into 3-nitro-*o*-toluamide, delicate needles, m. p. 158° , which is readily converted by Bouveault's method into 3-nitro-*o*-toluic acid, long, colourless needles or short rods, m. p. $151\text{--}152^{\circ}$ [the sodium (+ $3\cdot5\text{H}_2\text{O}$), barium (+ $3\text{H}_2\text{O}$),

and *silver* salts are described]. The acid cannot be directly esterified by methyl alcohol and hydrogen chloride, but the *methyl* (needles and leaflets, m. p. 50°) and *ethyl* (oily) esters are readily prepared by the action of the requisite alcohol on the acid *chloride*, m. p. 41°. 3-Nitro-*o*-toluic anhydride forms six-sided plates, m. p. 174°.

3-Nitro-*o*-toluamide is converted by prolonged treatment with boiling hydriodic acid into carbon dioxide and *m*-toluidine; when reduced with tin and hydrochloric acid it yields 3-methylbenziso-oxazole-3-one, slender needles, m. p. 119—120° (decomp.), *m*-toluidine hydrochloride, and 3-amino-*o*-toluic acid hydrochloride; the free acid, needles, m. p. 125—126° (decomp.), may also be prepared by reduction of the nitro-acid with ferrous sulphate in ammoniacal solution. When heated with formamide, it is converted into 5-methylquinazole-4-one, long needles, m. p. 224°.

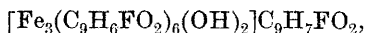
Ethyl nitrotoluoilmalonate, $\text{C}_6\text{H}_3\text{Me}(\text{NO}_2)\cdot\text{CO}\cdot\text{CH}(\text{CO}_2\text{Et})_2$, prisms, m. p. 60°, is prepared by the action of 3-nitro-*o*-toluoyl chloride on ethyl sodiomalonate, and yields a *potassium* derivative, $\text{C}_{15}\text{H}_{16}\text{O}_7\text{NK}$, yellow, silky needles. When boiled with hydriodic acid and red phosphorus, it gives 2:4-dihydroxy-5-methylquinoline, microcrystalline powder, which does not melt at 300°, and is converted by phosphoryl chloride into 2:4-dichloro-5-methylquinoline, long, slender needles, m. p. 132°. Treatment with tin and fuming hydrochloric acid transforms the dichloro-base into a mixture of 5-methyltetrahydroquinoline hydrochloride, needles and leaflets, m. p. 238—240° (the *nitroso*-derivative of the tetrahydro-base crystallises in shining, oblique prisms, m. p. 69—70°), and 5-methylquinoline, b. p. 263—264°/753 mm., 264—265°/765 mm. (picrate, m. p. 218—219°, methiodide, lemon-yellow needles and plates, m. p. 197° after softening at 193°); the latter base can also be obtained in small yield by distilling 2:4-dihydroxy-5-methylquinoline with zinc dust.

The following details of previously undescribed nitro- and amino-toluo-nitriles are given. 5-Nitro-*o*-toluo-nitrile (compare Mayer, *loc. cit.*), prepared from 5-nitro-*o*-toluidine in the manner used for the 3-isomeride, forms colourless leaflets, m. p. 100°, which are readily hydrolysed by a mixture of glacial acetic and fuming hydrochloric acids at 165°, to 5-nitro-*o*-toluic acid, m. p. 152—153°. The nitro-nitrile is readily reduced by stannous chloride and hydrochloric acid to 5-amino-*o*-toluo-nitrile, rhombic crystals, m. p. 90°. 6-Nitro-*m*-toluo-nitrile, m. p. 80°, is similarly reduced to 6-amino-*m*-toluo-nitrile, long, colourless needles, m. p. 95°. 5-Nitro-*m*-toluo-nitrile, needles, m. p. 104—105°, is prepared by the action of thionyl chloride on the corresponding *amide*, small needles, m. p. 164—165° (from 5-nitro-*m*-toluoyl chloride and ammonia in ethereal solution); 5-amino-*m*-toluo-nitrile forms needles, m. p. 75° (the *hydrochloride* is slowly volatile at 100°). 2-Nitro-*m*-toluo-nitrile, m. p. 84°, is reduced by hydriodic acid or ammonium sulphide to 2-amino-*m*-toluamide, m. p. 149°; by stannous chloride and hydrochloric acid to 2-amino-*m*-toluo-nitrile, m. p. 38°. II. W.

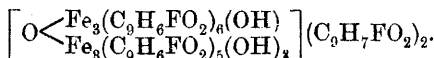
A Novel Application of Bromine Water in Synthetic Organic Chemistry.

JOHN READ and MARGARET MARY WILLIAMS (*J. Proc. Roy. Soc. N.S. Wales*, 1917, **51**, 558—564).—It has previously been shown (T., 1917, **111**, 240) that ethylene reacts directly with bromine water to give a good yield of ethylene bromohydrin. In the same way when air charged with bromine vapour is passed through a suspension of cinnamic acid in ice-cold water kept well stirred, a yield of over 80% of α -bromo- β -phenylhydracrylic acid is obtained, the other product being $\alpha\beta$ -dibromo- β -phenylpropionic acid. If the cinnamic acid is replaced by sodium cinnamate only 53% of the bromohydrin is obtained, and there is a third product, namely, β -bromostyrene, which accounts for 42.6% of the sodium cinnamate used. W. G.

Fluorocinnamic Acid. F. SWARTS (*Bull. Soc. chim.*, 1919, [iv], **25**, 325—335).—When benzaldehyde is slowly added to methyl fluoroacetate in the presence of sodium, the mixture being cooled below 0°, the principal product is *methyl fluorocinnamate*, m. p. 25°, b. p. 138°/23 mm., D^{25}_D 1.17258. It is readily saponified by aqueous potassium hydroxide, giving the *potassium salt*, from which, on acidifying, *fluorocinnamic acid*, m. p. 157.6° (corr.), b. p. 290°, is obtained. It yields *calcium*, *barium*, and *silver salts* and two complex *iron compounds* having the composition:



and

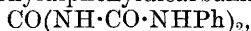


Fluorocinnamic acid is readily brominated, giving α -fluoro- $\alpha\beta$ -dibromo- β -phenylpropionic acid, m. p. 161.8°, giving a *barium salt* and a *methyl ester*, m. p. 120° (corr.). W. G.

Action of Ammonia and Amines on the Substituted Carbamides and Urethanes. I. Carbonyldiurethane.

F. B. DAINS, H. W. GREIDER, and C. H. KIDWELL (*J. Amer. Chem. Soc.*, 1919, **41**, 1004—1013).—Carbonyldiurethane, silky needles, m. p. 108°, is readily prepared by the addition of urethane (2 mols.) and pyridine (2 mols.) to a 10% solution of carbonyl chloride in benzene. It does not react with anhydrous liquid ammonia, but, in the presence of a little water, it gives carbethoxybiuret, m. p. 162—163°, traces of biuret, and cyanuric acid. No reaction occurs with cold alcoholic ammonia, but with aqueous ammonia (28%) the main reaction consists in the hydrolysis of one of the carbethoxy-groups, with the resulting production of ethyl allophanate, m. p. 192° (the *silver salt* is described); at the same time, carbethoxy-biuret is formed, but, being unstable in the ammonia solution, appears only as its decomposition product, cyanuric acid; biuret is formed only to a very limited extent. Ethyl allophanate is produced in 80% yield when ethylamine is used.

The course of the action of aniline on carbonyldiurethane depends largely on the temperature employed. At 110—115°, the products are diphenylbiuret, m. p. 210°, and phenylcarbethoxybiuret, $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$, m. p. 174° (the *sodium* and *silver* salts are described); the latter yields alcohol when dissolved in sodium hydroxide, and the solution on acidification gives phenylisocyanuric acid, fine needles, m. p. 290—300° for different preparations, which forms a *silver* and a *copper* salt. (Phenylcarbethoxybiuret and phenylisocyanuric acid, together with phenylurethane and phenylallophanic ester, are produced by the action of phenylcarbimide on urethane at 130°.) At 130—150°, the products are phenylcarbethoxybiuret, diphenylbiuret in a larger yield than before, and carbonyldiphenyldicarbamide,



m. p. 211°. At 170°, a little phenylcarbamide, m. p. 147°, and diphenylcarbamide, m. p. 235°, are also formed, and, at higher temperatures, the latter becomes the main product.

With *o*-toluidine at 130°, phenyldiurethane yields *o*-tolylcarbethoxybiuret, fine, colourless crystals, m. p. 155—156° (from which *o*-tolylisocyanuric acid, colourless needles, which do not melt below 300°, and yield a mono-*silver* salt, is obtained, as with the corresponding phenyl derivative), *di-o*-tolylbiuret, needles, m. p. 202—203°, and ethyl *o*-tolylallophanate, m. p. 137°. At 140°, the products are *o*-tolylcarbethoxybiuret, a little *di-o*-tolylcarbamide, and carbonyldi-*o*-tolyldicarbamide, m. p. 186°. At 170—180°, *di-o*-tolylbiuret, carbonyldi-*o*-tolyldicarbamide, *di-o*-tolylcarbamide, m. p. 248°, and *o*-tolylcarbamide, m. p. 188°, are obtained. *Di-o*-tolylcarbamide is the only substance isolated from experiments at 200°.

At 130—140°, β -naphthylamine yields mainly β -naphthylcarbethoxybiuret, colourless needles, m. p. 196° (β -naphthylisocyanuric acid has m. p. 290—291°), with small amounts of carbonyldi- β -naphthyldicarbamide, m. p. 293°. α -Naphthylamine, on the other hand, yielded at 130° mainly *di- α -naphthylcarbamide*, m. p. 280°; smaller amounts of α -naphthylcarbethoxybiuret, colourless needles, m. p. 198° (α -naphthylisocyanuric acid has m. p. 290°), and of *di- α -naphthylbiuret*, colourless crystals, m. p. 278—279°, were also produced.

The reactivity of carbonyldiurethane appears to be dependent on the presence of the carbonyl group, since neither methylenediurethane nor the substituted methylenediurethanes form metallic salts or react with amines. Thus, methylenediurethane is not attacked by aniline at 130°, traces of ammonia are evolved at 160°, and at 200° only a little diphenylcarbamide is obtained, which results from the slight dissociation of the urethane. The introduction of a phenyl group in the methylene radicle does not increase the reactivity of the substance, and, similarly, *o*-nitrophenylmethylenediurethane, colourless crystals, m. p. 190°, does not give an amide with ammonia or with aniline at temperatures up to 200°.

H. W.

Xylyloxyacetic Acids. W. GLUUD and P. K. BRENER (*Ges. Abhand. Kennt. Kohle*, 1917, **2**, 257—260; from *Chem. Zentr.*, 1919, i, 626).—Since the tolyloxyacetic acids are useful in the separation of the cresols of low temperature tars, the authors have investigated the corresponding compounds of the xylenols. *p*-Xylyloxyacetic acid, long, slender needles, m. p. 118°, is obtained in 35% yield by the action of chloroacetic acid on *p*-xylene in the presence of aqueous sodium hydroxide. The sodium salt is described. 4-*o*-Xylyloxyacetic acid, long, colourless needles or thin, rectangular plates, m. p. 162·5°, is similarly obtained in 63% yield; the sodium salt is crystalline. *m*-Xylyloxyacetic acid, long, white needles, m. p. 141·6°, is prepared in 51·5% yield. Ethyl *p*-tolylloxyacetate is obtained from ethyl chloroacetate and sodium *p*-tolylloxide; it is an oil, b. p. 142—143°/11 mm., which is converted by methyl-alcoholic ammonia into *p*-tolylloxyacetamide, m. p. 128°. H. W.

Trimethylene Disalicylate and Method of Preparing the Same. A. M. CLOVER (U.S. Pat. 1,286,944).—Trimethylene disalicylate, $\text{CH}_2(\text{CH}_2\cdot\text{CO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH})_2$, is prepared by the esterification of the glycol with twice its weight of salicylic acid in presence of half its weight of concentrated sulphuric acid at a temperature not exceeding 100°. Excess of unchanged acid is removed by washing the product with aqueous sodium carbonate at 50°, and the ester, which solidifies on cooling, is purified by crystallisation. It is a colourless, odourless substance of m. p. 77°, and has anti-rheumatic properties. G. F. M.

Some Aromatic β -Unsaturated Ketonic Acids. R. CIUSA (*Gazzetta*, 1919, **49**, i, 164—171).—Descriptions are given of a number of unsaturated ketonic acids, obtained by the condensation of pyruvic acid with aromatic aldehydes, $\text{R}\cdot\text{CHO} + \text{CH}_3\cdot\text{CO}\cdot\text{CO}_2\text{H} = \text{H}_2\text{O} + \text{R}\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{CO}_2\text{H}$.

Benzylidenepyruvic acid (compare A., 1910, i, 684) gives with phenylhydrazine a compound, m. p. 163—165° (Erlenmeyer, A., 1903, i, 698, gave m. p. 158°; 1904, i, 500), which dissolves in hot sodium carbonate solution, yields aniline when reduced with sodium amalgam, and is converted by boiling with glacial acetic acid in a reflux apparatus into a compound, m. p. 195° (decomp.), answering to Knorr's pyrazoline reaction; it must, therefore, be regarded as a true phenylhydrazone. The acid yields a dibromide, $\text{CHPhBr}\cdot\text{CHBr}\cdot\text{CO}\cdot\text{CO}_2\text{H}$, m. p. 124° (Erlenmeyer, *loc. cit.*, gave m. p. 138°, decomp.), decomposing at 166°. Benzylidenepyruvic acid *p*-nitrophenylhydrazone gives a crystalline sodium salt, which has been analysed.

Cinnamylidenepyruvic acid (*loc. cit.*; also Erlenmeyer, *loc. cit.*) yields a methyl ester, $\text{C}_{13}\text{H}_{12}\text{O}_3$, m. p. 126°, and a tetrabromide, $\text{CHPhBr}\cdot[\text{CHBr}]_3\cdot\text{CO}\cdot\text{CO}_2\text{H}$, which forms white needles, turning red at 200°, m. p. 218°. The ethyl ester forms (1) a tetrabromide, $\text{C}_{14}\text{H}_{14}\text{O}_3\text{Br}_4$, white needles, m. p. 118°, and a dibromide,

$C_{14}H_{14}O_3Br_2$, yellow needles, m. p. 86° . The phenylhydrazones of the acid and of its ethyl ester exhibit the behaviour of true hydrazones.

m-Nitrobenzylidenepyruvic acid, m. p. 111° (compare Baeyer and Drewsen, A., 1883, 341), forms a *sodium* salt ($+H_2O$) and a *dibromide*, $NO_2 \cdot C_6H_4 \cdot [CHBr]_2 \cdot CO \cdot CO_2H$, which crystallises in long, silky needles, m. p. 64° .

p-Nitrobenzylidenepyruvic acid, $C_{10}H_7O_5N$, forms shining, white needles, m. p. 117° . The *dibromide*, $NO_2 \cdot C_6H_4 \cdot [CHBr]_2 \cdot CO \cdot CO_2H$, crystallises in white needles, m. p. 78° .

Anisylidenepyruvic acid, $OMe \cdot C_6H_4 \cdot CH : CH \cdot CO \cdot CO_2H$, forms yellow needles, m. p. 81° , and crystallises from alcohol with $\frac{1}{3}Et \cdot OH$. Its *sodium* salt and its *dibromide*, $C_{11}H_{10}O_4Br_2$, crystallising in white scales, m. p. 125° , were prepared.

The compound, m. p. $137-138^\circ$, described by Ryan and Dunlea (A., 1913, i, 1067) as 5-phenyl-3-styryl*isooxazole* is probably the 3-phenyl-5-styryl*isooxazole* obtained by the author and Terni (A., 1911, i, 918), since the action of hydroxylamine on cinnamoylbenzoylmethane may result in the formation of two isomeric *isooxazoles*.

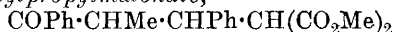
T. H. P.

The Isomeric Tropic Acids. ALEX. MCKENZIE and JOHN KERFOOT WOOD (T., 1919, 115, 828-840).

Preparation of 1:6-Dihydroxynaphthoyl-*o*-benzoic Acid and its Salts. GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 311213; from *Chem. Zentr.*, 1919, ii, 586).—1:6-Dihydroxynaphthalene is condensed with phthalic anhydride or phthalic acid in the presence of boric acid, and the acid is converted into its metallic salts by the usual methods; the presence of boric acid causes the reaction to result chiefly in the production of 1:6-*dihydroxynaphthoyl-*o*-benzoic acid*, whilst in the absence of a condensing agent or in the presence of substances such as zinc chloride, phthaleins are mainly or exclusively formed. 1:6-Dihydroxynaphthoyl-*o*-benzoic acid forms coarse crystals, m. p. $226-227^\circ$. The following salts are described: *monosodium* salt, pale yellow, flat prisms; the *disodium* salt is hygroscopic; *monopotassium* salt, yellow, rhombic or prismatic crystals; the *dipotassium* salt is sparingly soluble in alcohol or water; *monocalcium* salt, pale yellow, coarse crystals; *lead* salt, yellow, powdery precipitate; *copper* salt, green powder. 1:6-Dihydroxynaphthoyl-*o*-benzoic acid and its salts have a very sweet taste, whilst the corresponding 1:5-compound and its derivatives are tasteless. The new acid and its salts form a substitute for sugar and other sweetening agents, and also intermediate substances for the manufacture of dyes. When printed, as for chrome colours, 1:6-dihydroxynaphthoyl-*o*-benzoic acid gives bright greenish-yellow shades on cotton and wool which are fast to light and washing, whilst the corresponding 1:5-acid yields orange shades which are much less fast to light. H. W.

The cycloPropane Series. E. P. KOHLER and T. L. DAVIS (*J. Amer. Chem. Soc.*, 1919, **41**, 992—1001. Compare A., 1917, i, 566, 570; 1918, i, 72).—One of the most characteristic properties of cyclopropane derivatives is the ease with which the ring is opened by alkyloxides, with the production of a metallic derivative of an isomeric ethylenic ester. The action has been ascribed to the addition of the alkyloxide, followed by elimination of alcohol. In the present instance, the behaviour of methyl 2-phenyl-3-methyl-3-benzoylcyclopropanedicarboxylate has been investigated, since the elimination of alcohol is here impossible owing to the presence of the methyl group in position 3; the substance, however, does not appear to be appreciably affected by sodium methoxide.

The condensation of phenyl α -methylstyryl ketone and methyl malonate is best effected by means of a solution of sodium in dry methyl alcohol at the temperature of the steam-bath; the product consists of a mixture of the two stereoisomeric forms of *methyl γ -benzoyl- β -phenylpropylmalonate*,



(m. p.'s 91—93° and 88—90° respectively), in addition to a considerable amount of oil. Each of the esters can be hydrolysed to the corresponding *acid* (m. p. about 160°, and thick needles, m. p. 67°, respectively), from which the *γ -benzoyl- β -phenylvaleric acids* (silky needles, m. p. 115—117°, and small, transparent needles, m. p. 92—93°) are obtained by elimination of carbon dioxide; when treated with methyl alcohol and hydrogen chloride, these two acids yield the same *methyl ester*, large, rhomb-shaped prisms, m. p. 92° (which probably has the same configuration as the dibasic ester, m. p. 92°), whilst with bromine in carbon tetrachloride solution they give *γ -bromo- γ -benzoyl- β -phenylvaleric acid*, fine needles, m. p. about 160° (decomp.), from which *γ -benzoyl- β -phenyl- γ -methylbutyrolactone*, flat, six-sided plates, m. p. 93°, is obtained by the action of sodium carbonate.

The stereoisomeric methyl *γ -benzoyl- β -phenylpropylmalonates* readily react with bromine, yielding the same products, namely, a small amount of *methyl γ -bromo- γ -benzoyl- β -phenylpropylmalonate*, short, coarse needles, m. p. 114—115°, and an oil; the position of the bromine atom in the solid compound is deduced from its conversion into *methyl- γ -benzoyl- β -phenyl- γ -methylbutyrolactone-carboxylate*, colourless plates, m. p. 85°, when heated, and the identity of this substance with that obtained by the half-hydrolysis of the saturated ketonic ester and the action of bromine on the ester-acid. The action of potassium acetate on methyl *γ -bromo- γ -benzoyl- β -phenylpropylmalonate* yields *methyl 3-benzoyl-2-phenyl-3-methylcyclopropanedicarboxylate*, $(\text{CO}_2\text{Me})_2\text{C}$ $\begin{smallmatrix} \text{CHPh} \\ \text{CMeBz} \end{smallmatrix}$,

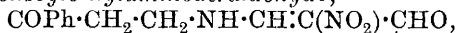
narrow prisms, m. p. 101°, which is not oxidised by permanganate, but is readily reduced by zinc dust and acetic acid, yielding the saturated ester, m. p. 91—93°, as sole product of the action. The ester acid, unlike the derivatives of cyclopropane previously studied, is insensitive to alkyl oxides except in the presence of moisture,

when it is hydrolysed to the corresponding *acid ester*, three-sided prisms, m. p. 162°. 3-Benzoyl-2-phenyl-3-methylcyclopropanedicarboxylic acid, needles, m. p. 176—178° (decomp.), is obtained by complete hydrolysis of the corresponding ester, into which it is reconverted through the silver salt; when treated with methyl alcohol and hydrogen chloride, on the other hand, the sole product is a very stable, crystalline compound, $C_{22}H_{26}O_7$, m. p. 158.5—159.5°.

The oily material obtained during the bromination of the methyl γ -benzoyl- β -phenylpropylmalonates was treated with potassium acetate, whereby a small further quantity of the cyclopropane ester already described, and an ethylenic isomeride, stout needles, m. p. 129—131°, were isolated; the latter is not reduced by zinc dust and acetic acid, and hence is not a cyclopropane derivative. Its most characteristic property is the readiness with which it is transformed by bases or mineral acids into an isomeric *ester*, hexagonal plates, m. p. 145°. On hydrolysis, it yields an *ester acid*, needles, m. p. about 189° (decomp.), and a dibasic acid, needles, m. p. about 180° (decomp.); these compounds, however, are probably derivatives of the ester, m. p. 145°, since this ester is obtained when the acid is esterified either by the silver salt method or by methyl alcohol and hydrogen chloride. H. W.

Condensation of Phenyl β -Aminoethyl Ketone with Nitromalonaldehyde. WILLIAM J. HALE and EDGAR C. BRITTON (*J. Amer. Chem. Soc.*, 1919, **41**, 1020—1026).—In continuation of the work of Hale and Hoyt (A., 1916, i, 71) and of Hale and Honan (this vol., i,), the condensation of sodium nitromalonaldehyde with a methylene group activated by the presence of a neighbouring carbonyl group has been studied.

α -Nitro- β -benzoylethylaminoacetaldehyde,

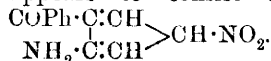


small prisms, m. p. 153°, is readily produced when an aqueous solution of molar quantities of sodium nitromalonaldehyde and phenyl β -aminoethyl ketone hydrochloride is maintained at 50° for some hours. When twice the relative amount of the amino-ketone hydrochloride is used and the solution is treated with a little sodium hydroxide, β -nitro- α -benzoylethylamino- γ -benzoylethyliminopropylene, $COPh \cdot [CH_2]_2 \cdot NH \cdot CH : C(NO_2) \cdot CH : N \cdot [CH_2]_2 \cdot COPh$, colourless clusters of needles, m. p. 145° (*platinichloride*, m. p. 208°), is produced, which is decomposed by boiling concentrated hydrochloric acid into the nitroacetaldehyde, m. p. 153°, and phenyl β -aminoethyl ketone; the compound can also be obtained by addition of sodium hydroxide to an aqueous solution of the nitroac-

aldehyde. 4-Nitro-3-phenacylpyrrole,
$$\begin{array}{c} C(NO_2) = CH \\ | \\ CH : C(CH_2 \cdot COPh) \end{array} > NH,$$

is formed by the condensation of phenyl β -aminoethyl ketone hydrochloride and sodium nitromalonaldehyde in aqueous-alcoholic solution in the presence of sodium hydroxide, or from benzoylethylaminonitroacetaldehyde under similar conditions; it forms small,

lemon-yellow prisms, m. p. 170° (the *platinichloride* decomposes above 300° without melting). Attempts to oxidise the substance to a nitropyrrolecarboxylic acid were unsuccessful. The yield of the pyrrole derivative is only moderate, and the alkaline mother liquors from the preparation yield, on acidification, a red, amorphous precipitate, decomposing between 127° and 132° , which appears to consist of 3-nitro-5-amino-1-benzoylcyclopentadiene,

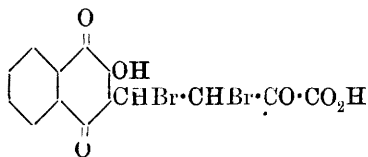


H. W.

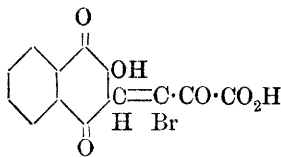
Condensation of Deoxybenzoin and Aldehydes. ANANDA KISORE DAS and BROJENDRA NATH GHOSH (T., 1919, 115, 817—820).

Condensation of Deoxybenzoin with Aromatic Aldehydes. BAWA KARTAR SINGH and JATINDRA KUMAR MAZUMDAR (T., 1919, 115, 821—825).

Action of Potassium Ferricyanide on Alizarin in Alkaline Solution. II. R. SCHOLL and A. ZINKE (*Ber.*, 1919, 52, [B], 1142—1160. Compare this vol., i, 25).—Addition of bromine to hydroxynaphthaquinonylvinyglyoxylic acid leads to the formation of β -[2-hydroxy-1 : 4-naphthaquinonyl-3-vinyglyoxylic acid dibromide (I), m. p. about 150° (decomp.) after softening at about 83° , which slowly loses hydrogen bromide at the ordinary temperature and forms a mixture of cumaroid (α) (II) and *cumaroid* (β)

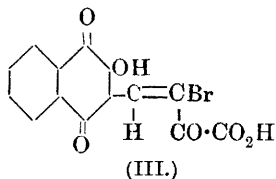


(I.)



(II.)

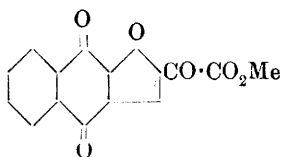
β -[2-hydroxy-1 : 4-naphthaquinonyl-3]- α -bromovinylglyoxylic acids (III), which could not be separated owing to their instability.



(III.)

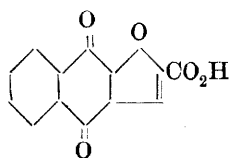
Cumaroid Series.—Methyl β -[2-hydroxy-1 : 4-naphthaquinonyl-3]- α -bromovinylglyoxylate, yellow prisms, m. p. 217° (decomp.), is obtained mixed with methyl naphthafurylquinonylglyoxylate by the action of boiling methyl alcohol on the crude dibromide; the *acetyl* derivative forms pale yellow, shining leaflets, m. p. 188 — 189° . The *ethyl* ester has m. p. 158° . Cautious hydrolysis of the methyl ester yields the corresponding acid, m. p. 171 — 172° (decomp.) after previous darkening and softening, which is transformed by boiling water into naphthafuranquinone (see later), and by boiling xylene into a crystalline acid, m. p. about 251 — 252° . When heated alone at 100° or with alcohol, it is converted into bromobenzcumarinquinone. When

treated with methyl alcohol and hydrogen chloride, it re-forms the methyl ester, m. p. 216—217°.



Methyl β-naphthafuryl-3:8-quinone-1-glyoxylate (annexed formula) crystallises in reddish-yellow needles, m. p. 222—223°, whilst the corresponding *ethyl* ester forms reddish-yellow needles, m. p. 187° (*phenylhydrazone*, brown needles, m. p. about 208—210°); the latter is oxidised by dilute nitric acid at 200° to phthalic acid. The

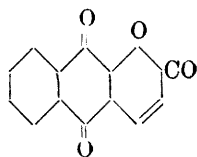
esters are converted by methyl-alcoholic potassium hydroxide into a green salt, which is rapidly oxidised by air to a red salt, the latter being derived from naphthafuranquinonecarboxylic acid (annexed formula), the former from its



dihydro-derivative. The acid itself forms red crystals, m. p. 298°, and yields a *sodium* salt which dissolves sparingly in water. When distilled alone or, preferably, with lime, it passes into *β-naphthafuran-3:8-quinone* (3:4-*phthalylfuran*), m. p. 210°, which is also

obtained by boiling crude hydroxynaphthaquinonylbromovinylglyoxylic acid or pure *β*-hydroxynaphthaquinonyl-*α*-bromovinylglyoxylic acid with water. It yields a *mono-phenylhydrazone*, purple needles, m. p. 158—159°, and a *dibromide*, reddish-yellow crystals, m. p. 112—114° (decomp.), after previous softening, which slowly loses hydrogen bromide at the ordinary temperature. When boiled with glacial acetic acid, the dibromide is converted into a mixture of 1- and 2-*bromonaphthafuranquinones*, yellowish-red leaflets and red needles, m. p. 167—168°, after much softening.

Cumarinoid



Series.—4 : 5-Benzcumarin-3 : 6-quinone (3 : 4-*phthalyl-α-pyrone*) (annexed formula), brownish-yellow crystals, m. p. 214—215°, is obtained by cautiously heating silver hydroxynaphthaquinonylvinyglyoxylate in a current of carbon dioxide. 1-Bromo-4 : 5-benzcumarin-3:6-quinone is prepared by the action of boiling alcohol on crude hydroxynaphthaquinonylbromovinylglyoxylic acid; it forms yellowish-brown needles,

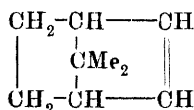
m. p. 224—225°.

2:2-Dibromo-1:3-diketohydrindene, m. p. 175—177°, is obtained by the action of an excess of boiling bromine water on hydroxynaphthaquinonylvinyglyoxylic acid. H. W.

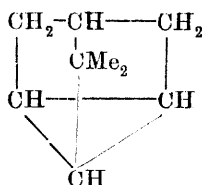
The Basic Properties of Phenanthraquinone. JOSEPH KNOX and HELEN REID WILL (T., 1919, 115, 850—852).

Studies in the Camphane Series. XXXVII. Aryl Derivatives of Imino- and Amino-camphor. MARTIN ONSLOW FORSTER and HANS SPINNER (T., 1919, 115, 889—895).

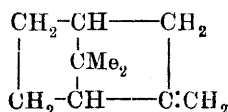
Ozonisation of *apo*Bornylene and of the different Fenchenes. Constitution of these Hydrocarbons. R. H. ROSCHIER (*Acad. Sci. Fennicae*, 1919, [A], 10, 1—83; from *Chem. Zentr.*, 1919, i, 726—730. Compare Komppa and Hentikka, A., 1912, i, 278; 1914, i, 557).—*apo*Bornylene is a mixture of two isomeric hydrocarbons, one of which is the actual *apobornylene* (I), whilst the other is tricyclic *apocyclene* (II). Fenchene is a mixture of at least five terpenes, two of which are semicyclic, two endocyclic, and one tricyclic. Ozonisation of *d*-fenchene (Wallach's *D-l*-fenchene) has confirmed the formula (III) for it, whilst the formula IV may be ascribed with certainty to β -fenchene (Wallach's *D-d*-fenchene and Semmler's *isofenchene*). The fenchene, b. p. 145—147°, is mainly ring-unsaturated, and probably has the constitution (V). The fenchene of lowest boiling point is identical with Semmler's *isoallofenchene* (VI). A small amount of *cyclofenchene* (VII) identical with Aschan's β -pinolene is contained in the fractions of fenchene of lowest boiling point.



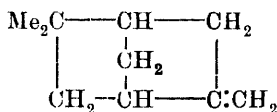
(I.)



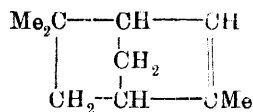
(II.)



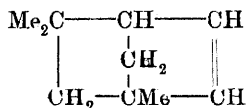
(III.)



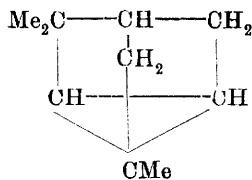
(IV.)



(V.)



(VI.)



(VII.)

*apo*Bornylene was prepared from camphenilole by the xanthate method and from camphenilone through the dichloride; the product obtained by the first method was a completely solid, viscous, camphoraceous mass, m. p. 38°, b. p. 138°/760 mm., whilst that obtained by the second process, b. p. 138—139°, was oily at the ordinary temperature, but solidified when moderately cooled. Attempts to prepare *apobornylene* by the distillation of

camphenylamine phosphate in a current of carbon dioxide were unsuccessful, the original amine being recovered. Ozonisation of *apobornylene* yielded a normal *ozonide*, $C_9H_{14}O_3$, voluminous, white powder, m. p. 55° (decomp.), which became transformed into a brown oil after some months; it decomposes quietly when heated. Fission of the *ozonide* by warming its solution in acetic acid yielded mainly three fractions; the most volatile was an oil, which did not reduce Fehling's solution, gave no semicarbazone, and probably consisted of *apocyclene acetate*. The middle fraction was aldehydic, but contained some peroxide; it could not be purified by means of a crystalline semicarbazone. The *apobornylenedialdehyde* was so unstable that it became resinified for the most part during distillation, and was converted into *apocamphoric acid* by treatment with potassium carbonate. *apoCamphoric anhydride*, m. p. $174-175^\circ$, was obtained from the least volatile fraction.

When the *ozonide* of *apobornylene* obtained from camphenylone dichloride was decomposed in acetic acid solution and the latter was distilled, the distillate was found to contain *apocyclene* (20–30% of the *apobornylene* taken); the latter is not attacked by ozone, and is extraordinarily stable towards permanganate. It is a readily volatile, crystalline substance with a sweetish, but rather irritating, odour. It has m. p. $42.5-43^\circ$, b. p. $138-139^\circ/764$ mm., D_4^{40} 0.8710, n_D^{40} 1.45144, mol. ref. 37.80 (calc. for tricyclic, C_9H_{14} , 37.16), n_a^{40} 1.44910, n_β^{40} 1.45686, n_γ^{40} 1.46190. *apo-Bornylene*, obtained by the xanthate process, contained 62% of *apocyclene*. Treatment with acetic acid in the presence of sulphuric acid converted *apocyclene* into the acetate, b. p. $81-82^\circ/8$ mm., D_4^{20} 0.9971, n_D^{20} 1.4623, n_a^{20} 1.4601, n_γ^{20} 1.4729. It was hydrolysed to an alcohol, which was not obtained in a state of purity owing to lack of material, but which was identified as β -fenchocamphorol by its oxidation through β -fenchocamphorone to *apofenchocamphoric acid*; the latter could be separated into *trans-apofenchocamphoric acid*, m. p. $144-145^\circ$, and β -fenchocamphorone, m. p. $60-63^\circ$, characterised by its semicarbazone, m. p. $200-201^\circ$.

The α -fenchene was obtained from fenchyl chloride, and had b. p. $155-160^\circ$, $D_4^{7.5}$ 0.8670, $n_D^{17.5}$ 1.46729, $\alpha_D^{20} -32.32$. The *ozonide* was a viscous, colourless oil which did not explode when heated, and contained more highly oxygenated products than the normal *ozonide*. After fission, it yielded about 50% of α -fenchocamphorone (identical with Wallach's *Dd*-fenchocamphorone), b. p. $198-200^\circ$ (semicarbazone, m. p. $220-221^\circ$). In addition, there were formed a neutral, aldehydic, yellow oil, b. p. $120-133^\circ$, which could not be purified, and α -fenchenylic acid (7:7-dimethyl-1:2:2-bicycloheptane-2-carboxylic acid), m. p. $71.5-72^\circ$. The zinc salt is less soluble in hot than in cold water; the *anilide* forms silky needles, m. p. $149.5-150^\circ$.

The specimen of β -fenchene employed was obtained by distillation of *r*-fenchyl alcohol with potassium or sodium hydrogen sulphate in a current of carbon dioxide. It was separated into

three fractions by repeated distillation, the most volatile of which was purely endocyclic, the least volatile purely semicyclic, according to optical analysis; β -fenchene was contained in the fraction, b. p. 151—153°. β -Fenchene ozonide forms a viscous, syrupy oil which contains more highly oxygenated products than the normal ozonide. Fission yielded impure fenchocamphorone, which was identified by its semicarbazone, m. p. 193—195°; further oxidation of the liquid ketone led to the isolation of a little apocamphoric anhydride (thus proving the presence of α -fenchocamphorone as impurity), and mainly to apofenchocamphoric acid (4:4-dimethylcyclopentane-1:3-dicarboxylic acid), prisms or monoclinic plates, m. p. 144—145°; since the acid cannot be converted into an anhydride in the usual manner, it must be a *trans*-form; the zinc salt, which is less soluble in hot than in cold water, is very characteristic.

The intermediate fraction of the hydrocarbon mixture, b. p. 145—147°, behaved on ozonisation as a compound unsaturated in the ring. It is a mixture of two hydrocarbons, one of which is *isoallofenchene* (VI), whilst the other probably has the constitution V. Fission of the ozonide yielded mainly a dialdehyde and a keto-acid. The dialdehyde, $C_{10}H_{16}O_2$, is a mobile, yellow oil, b. p. 118—120°/10 mm., D_4^{20} 1.0215, n_D^{20} 1.4700, n_s 1.4677, n_r 1.4815, which is very unstable when exposed to air, and could not be isolated in the pure state; its *disemicarbazone* crystallises in fine granules, m. p. 219°. The crude aldehyde fraction contained also a small quantity of *r-cis-isofenchocamphoric* acid. The keto-acid, $C_{10}H_{16}O_3$, forms a viscous, yellow oil, D_4^{20} 1.0924, n_D^{20} 1.4774, which could not be caused to crystallise, and was purified by means of its *semicarbazone*, m. p. 220—221°; it contains the -COMe group, since, when treated with bromine and alkali, it yields bromoform and a dibasic acid, $C_9H_{14}O_4$, prisms, m. p. 147—148°, which, contrary to expectation, is not identical with apofenchocamphoric acid obtained by the oxidation of β -fenchocamphorone. Full investigation of the acid was impossible owing to the small amount of available material, but its properties show it to be *cis-apofenchocamphoric* acid.

Fission of the ozonide obtained from the most volatile fraction of the β -fenchene hydrocarbon mixture yielded aldehydic and acidic components, together with a small amount of a pleasant-smelling, oily ketone, $C_9H_{14}O$ (*semicarbazone*, m. p. 209°), which could be oxidised to an acid, probably $C_9H_{14}O_4$. The substances could not, however, be fully investigated owing to lack of material. The acidic fraction contained the keto-acid described above in small amount, together with *r-cis-isofenchocamphoric* acid, m. p. 173—174°, and an aldehydic acid which, on further oxidation, was transformed into *cis-isofenchocamphoric* acid, thus showing the fraction to consist mainly of *isoallofenchene* (VI).

The small portion of this fraction which was not attacked by ozonisation consisted of the hydrocarbon, *cyclofenchene*, $C_{10}H_{16}$, b. p. 142—143°, $D_4^{18.5}$ 0.8624, $n_D^{18.5}$ 1.45364, mol. ref. 42.73. It is

shown to be identical with Aschan's β -pinolene (VII) by its conversion into the hydrochloride, m. p. 26—28°. The *hydrobromide* has m. p. 4°, b. p. 92—93°/12 mm., D_4^{20} 1.2389, n_D^{20} 1.50570, mol. ref. 52.04. Like β -pinolene, it could be converted through the acetate into *isofenchyl* alcohol, *isofenchone*, and *r-isofenchocamphoric* acid.

H. W.

Behaviour of an Alcoholic Solution of Lead Acetate towards the Resinous Substances of Colophony. I. LUDWIG PAUL (*Kolloid Zeitsch.*, 1919, **24**, 95—104, 129—138, 165—173).—

The first section of this paper deals with the previously published work of Tschirch ("Die Harz und Harzbehälter," Berlin, 1906). A résumé of the results and conclusions drawn is given, and these are critically discussed. In the third section experiments on the behaviour of the resinous substances of colophony are described. A solution of powdered colophony is made in 5% sodium hydroxide, which on treatment with sodium chloride solution deposits greyish-white needles; the mother liquor, on treatment with hydrochloric acid, gives a precipitate which after washing is practically all soluble in water. On precipitating this solution with a few drops of hydrochloric acid, an acid, m. p. 123°, is precipitated. This is β -*KLw*-resin acid (colophony water soluble resin-acid). The behaviour of the various solutions of colophony with alcoholic solutions of lead acetate is also studied, and it is shown that the starting material in all previous investigations is the colloidal substance γ -pinic acid, m. p. 75—76°. This substance is slowly decomposed by the bound colloidal water in boiling alcoholic solutions. The colloidal behaviour of the components of colophony, particularly in their changes, is probably due to special holding power which resinous substances are able to exert on one another, and thereby an apparent formation of new chemical substances occurs. The residue from the *KL* substances soluble in sodium hydroxide furnishes an example of this type of substance. These extraction residues must not be confused with the decomposition products, which are obtained on washing, through the changes occurring in β -pinic acid, m. p. 98—100°, and those are probably the substances from which fossil resins are produced. Just as the resinous substances often form weak, but well-crystallised, compounds with hydrocarbons by virtue of the holding power mentioned above, so γ -pinic acid forms similar weak compounds with ethereal oils which constitute the turpentine resins. The method used by Tschirch leads to new substances which are not present in the original material. This is particularly the case for a series of amorphous substances of low melting point isolated by Tschirch from recent fossil resins. A method of separation, due to Tschirch, which leads to the acceptance of three abietic acids (α , β , and γ) is to be regarded in the above sense. Although the use of alcoholic lead acetate does not destroy the colloidal condition of the substances treated with it, for example, in the case of γ -pinic acid, yet a change in the so-called colloidal constitution is to be observed. Under the term colloidal constitution the author

understands the method of combination and the number of molecules of colloidal water in the molecule; these are distinguishable by the tannoid properties of the corresponding resin soaps and by the decomposition and associating properties of the free resin acids. Just as γ -pinic acid retains its colloidal water under treatment with lead acetate, so γ -pinic acid in its weak hydrocarbon compounds retains the hydrocarbon when precipitated by the same reagent. True resinous substances are to be distinguished from resin-like substances. The former differ from the latter in their power of passing into crystalline substances, the so-called absolute resins, whereas the latter are not crystallisable. The colophony substance is, in consequence of its colloidal nature, a living substance, which does not come to rest until the colloidal water is used up and thereby a labile equilibrium is set up. The stable condition is probably reached in amber. J. F. S.

The Mutual Influence on the Electrolytic Conductivity of Gallotannic Acid and Boric Acid in Connexion with the Composition of the Tannins. J. BÖSEKEN and W. M. DEERNS (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 907—910).—The researches of E. Fischer have shown that the tannin of the gall nut consists principally of a mixture of the pentadigalloyl ethers of α - and β -glucose, and if this is the case the influence of the conductivity of this substance on that of boric acid should be considerable. Experiments have therefore been performed on the conductivity of solutions of methyl gallate and of the tannin of the gall nut in the presence of boric acid; the increase in conductivity is very considerable and markedly higher in the case of the tannin than in that of the methyl ester, thus agreeing with the presence in the tannin of ten pairs of favourably situated hydroxyl groups in every molecule. H. W.

Tannins. II. Chebolic Acid. KARL FREUDENBERG (*Ber.*, 1919, **52**, [B], 1238—1246).—Chebolic acid is a moderately strong acid in which the presence of a free carboxyl group has previously been assumed, and this hypothesis is now further confirmed. It cannot be hydrolysed by tannase, probably on account of the inhibiting action of the acid group. When heated in aqueous solution, the acidity increases, particularly at first, far more rapidly than is required by the gallic acid eliminated, so that a second, unknown acid appears to be first liberated. This is shown to be the case, since after removal of gallic acid with ether, neutralisation of the solution, and extraction of a crystalline tannin with ethyl acetate, an apparently new, phenolcarboxylic acid can be isolated in the form of its thallium *salt*; analyses of the latter have not yet yielded absolutely concordant results, but it appears to contain 5—6% of water and to approximate in composition to thallium gallate; it has $[\alpha]_D^{20} + 34^\circ (\pm 4^\circ)$ in water. The crystalline tannin, mentioned above, has $[\alpha]_D^{18} + 85^\circ (\pm 4^\circ)$ in alcoholic solution, and appears to be a digalloyl glucose. Further work on chebolic acid is promised, but the results so far obtained seem to indicate that the

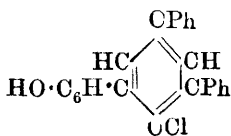
glucose is esterified with two molecules of gallic acid, and that the new acid is not attached to the glucose residue through its carboxyl group, which is free, but probably by a glucosidic linking.

The use of thallium carbonate or hydroxide for the neutralisation of solutions after hydrolysis appears very advantageous, since it can readily be removed by addition of halogen acid, and, in this particular instance, it also effects the precipitation of highly-coloured impurities.

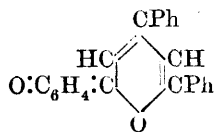
H. W.

Pyrylium Compounds. IV. Hydroxypyryonium Salts, their Pseudo- and Anhydro-bases. W. DILTHEY (*Ber.*, 1919, 52, [B], 1195—1207).—The previous work (A., 1917, i, 578, 660) has been extended to the anthocyanidines.

Phenyl styryl ketone and *p*-methoxyacetophenone react with ferric chloride in acetic anhydride solution to yield the *iron* salt, $C_{24}H_{19}O_2Cl_4Fe$, red prisms, m. p. 254—255°, which is converted by sodium carbonate into α -hydroxy- γ -*diphenyl*- α -*p*-anisyl- Δ^{γ} -pentadien- ϵ -one, $OMe \cdot C_6H_4 \cdot C(OH) : CH \cdot CPh : CH \cdot CPh$, almost colourless, transparent prisms, m. p. 105—106° (*picrate*, slender, orange needles, m. p. 237—238°), which is slowly attacked by boiling alcoholic potassium hydroxide solution, yielding anisic acid. Demethylation of the enol is effected by hydrochloric acid at 160°, whereby 2:4-*diphenyl*-6-*p*-hydroxyphenylpyrylium chloride (annexed formula) is formed in dark yellowish-red prisms, m. p. 293—294°.

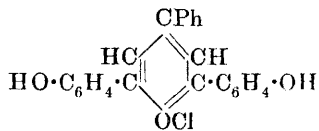


When a solution of this salt in pyridine is treated with alcohol and much water, it yields α -hydroxy- γ -*diphenyl*- α -*p*-hydroxyphenyl- Δ^{γ} -pentadien- ϵ -one, slender, yellow needles, which darken when heated and have the same m. p. as the *anhydro-base*; the latter (annexed formula) which is best prepared by the action of heat on the enol, forms violet-blue aggregates, m. p. 164°.



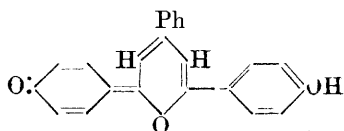
p-Hydroxyphenyl styryl ketone condenses with *p*-hydroxyacetophenone in the presence of zinc chloride and acetic anhydride to yield a complex zinc salt, from which the *platinichloride*, $C_{54}H_{42}O_{10}Cl_6Pt$, microscopic, orange needles, m. p. 258—259°, is obtained by double decomposition; the zinc salt is transformed by sodium acetate into the *diacetyl compound* of the *pseudo-base*,

$OAc \cdot C_6H_4 \cdot C(OH) : CH \cdot CPh : CH \cdot CO \cdot C_6H_4 \cdot OAc$, almost colourless, silky needles, m. p. 122° (*acid picrate*, long, yellow needles, m. p. 232—234°; *perchlorate*, orange-yellow, six-sided platelets, m. p. 249—250°).



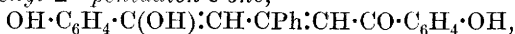
When treated with hot hydrochloric acid, the acetyl groups are removed, the *chloride* of the cyclic base being formed (annexed formula); it forms very stable, orange leaflets ($+ \frac{1}{2}H_2O$), which do not melt below 320°. It may

also be prepared by demethylation of α -hydroxy- γ -phenyl- α -di-*p*-anisyl- $\Delta^{\alpha\gamma}$ -pentadien- ϵ -one with hydrochloric acid at 160°. The corre-



sponding perchlorate ($+ \frac{1}{2} \text{H}_2\text{O}$) has m. p. 296—298°. The *anhydro*-base (annexed formula), slender needles, decomposing at about 340°, is conveniently prepared by addition of sodium carbonate to a solution of

the perchlorate or *sulphate*, the chloride being too sparingly soluble for this purpose. When a solution of the base in pyridine is cautiously treated with alcohol and water, α -hydroxy- γ -phenyl- α -di-*p*-hydroxyphenyl- $\Delta^{\alpha\gamma}$ -pentadien- ϵ -one,



is precipitated in almost colourless, coarse needles which do not show a definite melting point; when heated at 130—140° it is re-converted into the anhydro-base.

H. W.

Cryptopine. II. WILLIAM HENRY PERKIN, jun. (T., 1919, 115, 713—790).

A New Method for a Separate Extraction of Hydrastine and Berberine from Golden Seal on a large Scale. ELSA SCHMIDT (*Amer. J. Pharm.*, 1919, 91, 270—275).—Hydrastine is extracted from golden seal by percolation with benzene containing a trace of ammonia, and is isolated by extracting with 3% sulphuric acid and precipitating with ammonia. From the residual drug berberine is extracted by percolation with dilute aqueous acetic acid, and isolated as its hydrochloride by adding hydrochloric acid to the percolate. The author reviews the properties and uses of the two alkaloids, and the methods available for their detection and estimation.

G. F. M.

Action of Hydrogen Peroxide on Sparteine and isoSparteine. AMAND VALEUR and E. LUCE (*Compt. rend.*, 1919, 168, 1276—1278).—Sparteine dioxide, $\text{C}_{15}\text{H}_{26}\text{O}_2\text{N}_2$, obtained by the action of hydrogen peroxide (compare Wackernagel and Wolfenstein, A., 1904, i, 917), is a strong base. Its hydriodide is not decomposed by potassium hydroxide as stated by Ahrens (compare A., 1887, 1056; 1891, 842; 1893, i, 232), but, on the other hand, the base in cold concentrated aqueous solution decomposes potassium iodide. The hydriodide, $\text{C}_{15}\text{H}_{26}\text{O}_2\text{N}_2\text{HI}$, is reduced by hydriodic acid, giving *N*-hydroxysparteine periodide, $\text{C}_{15}\text{H}_{26}\text{N}_2(\text{OH})\text{I}_2$, m. p. 134°, which on further reduction gives a *sparteine periodide*, $\text{C}_{15}\text{H}_{26}\text{N}_2 \cdot 2\text{HI} \cdot \text{I}_2$, m. p. 187°. The *hydriodide of hydroxysparteine iodide*, $\text{C}_{15}\text{H}_{26}\text{N}_2(\text{OH})\text{I} \cdot \text{HI}$, has m. p. 256—260°. Sparteine dioxide gives a *methiodide*, $\text{C}_{15}\text{H}_{26}\text{ON}_2(\text{OMe})\text{I}$, m. p. 130°, which on reduction loses its methoxy-group and gives sparteine.

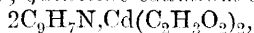
isoSparteine resembles sparteine in its behaviour towards hydrogen peroxide. It yields *isosparteine dioxide*, m. p. 115·5°, a strong

base, which decomposes potassium iodide in concentrated solutions giving an *iodide*, $C_{15}H_{26}ON_3(OH)I \cdot 2H_2O$, m. p. 83° . The corresponding *bromide* has m. p. $107-109.5^\circ$. W. G.

The Constitution of Surinamine. E. WINTERSTEIN (*Zeitsch. physiol. Chem.*, 1919, **105**, 20-24).—The author agrees with Goldschmidt (A., 1913, i, 643) that surinamine is *N*-methyltyrosine. He prepared the latter substance by the method of Friedmann and Gutmann (A., 1910, i, 741), and found that no toxic action followed the administration of 0.5 gram to a rabbit or 1 gram daily to a dog.

Surinamine (ratanhine), according to Goldschmidt, is optically active, $[\alpha]_D = -18.6^\circ$. An attempt to resolve the synthetic and inactive compound by the aid of *Penicillium* was unsuccessful. By subjecting the *N*-methyltyrosine to the action of putrefactive organisms a base was formed which was identified as *p*-hydroxyphenylethylmethylamine. J. C. D.

New Additive Compounds of Quinoline with certain Inorganic Salts. JAMES H. WALTON and CHUAN LING LIANG (*J. Amer. Chem. Soc.*, 1919, **41**, 1027-1028).—The following compounds were obtained by saturating synthetic quinoline with the requisite salt at 100° , allowing the solution to cool to the temperature of the room, and separating the crystals: *Quinoline silver thiocyanate*, $2C_9H_7N \cdot AgSCN$, small, white crystals; *quinoline mercuric thiocyanate*, $2C_9H_7N \cdot Hg(SCN)_2$, pale yellow crystals; *quinoline mercurous thiocyanate*, $2C_9H_7N \cdot HgSCN$, small, colourless, shining crystals; *quinoline cupric thiocyanate*, $3C_9H_7N \cdot 2Cu(SCN)_2$, small, yellow crystals; *quinoline cuprous thiocyanate*, $2C_9H_7N \cdot CuSCN$, yellow needles; *quinoline zinc acetate*, $C_9H_7N \cdot Zn(C_2H_3O_2)_2$, colourless, crystalline powder; *quinoline cadmium acetate*,



colourless, crystalline powder. Manganese and cobalt acetates are also readily soluble in quinoline, but do not appear to form additive compounds under the experimental conditions used. H. W.

Intermediates used in the Preparation of Photosensitising Dyes. I. Quinoline Bases. L. A. MIKESKA, J. K. STEWART, and LOUIS E. WISE (*J. Ind. Eng. Chem.*, 1919, **11**, 456-458).—The parent bases required for the production of the photosensitising dyes, pinaverdol, pinacyanol, and dicyanine are quinoline, 2-methylquinoline, and 2:6- and 2:4-dimethylquinolines. The well-known methods by which these bases may be prepared from aniline or toluidine have been investigated and certain modifications are proposed, which make it possible to work successfully with hundreds of grams of reagents at a time. The chief innovation is that extractions with ether are employed instead of steam distillations. J. C. W.

Intermediates used in the Preparation of Photosensitising Dyes. II. Quaternary Haloids. CARL H. LUND and LOUIS E. WISE (*J. Ind. Eng. Chem.*, 1919, **11**, 458-460).—The quinoline

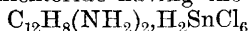
bases mentioned in the preceding abstract are treated with an equimolecular quantity of methyl or ethyl iodide in a round-bottomed flask connected with a reflux condenser, care being taken to modify the reaction by cooling when it has once set in, except in the case of the bases with methyl in position 2, which require prolonged heating on a water-bath. The quaternary iodides obtained by the authors usually melted at the published temperatures, but higher figures are given for 2:6-dimethylquinoline methiodide, m. p. 246—247°, and 2:4-dimethylquinoline ethiodide, m. p. 223—225°.

J. C. W.

Synthesis of Photosensitising Dyes. Pinaverdol and Pinacyanol. LOUIS E. WISE, ELLIOT Q. ADAMS, J. K. STEWART, and CARL H. LUND (*J. Ind. Eng. Chem.*, 1919, **11**, 460—463).—The authors have prepared about fifteen dyes of this type by following the instructions of the original German patents (D.R.-P. 167159 of 1903 and 172118 of 1905). A product which they designate *Pv* 1 is identical with the German pinaverdol or the sensitol-green of the Ilford Co. It is made by slowly adding sodium methoxide solution to a solution of dry quinoline methiodide in boiling methyl alcohol, and allowing to cool slowly. It resembles splinters of brass in appearance, the crystals being monoclinic; $a:b:c=1.1014:1:1.6053$, $\beta=88^{\circ}20'$. Another product, *Pc IX*, is identical with pinacyanol or sensitol-red. It is obtained by adding a mixture of sodium hydroxide and formalin to a boiling alcoholic solution of quinoline and quinaldine ethiodides, air being first expelled, then diluting somewhat with boiling water and allowing to cool slowly. It crystallises in lustrous, bluish-green needles. There is no real evidence that quinoline ethiodide enters into the reaction at all, and if it is replaced by potassium iodide, a dye, *Pc X*, is formed, although in poor yield, which is very probably identical with *Pc IX*. Like *Pv* 1, *Pc IX* is a quaternary iodide. If transformed into the chloride by reaction with silver chloride in concentrated hydrochloric acid, it gives *Pc XII*, which is more soluble than the iodide. Absorption curves are reproduced in the original.

J. C. W.

Benzidine Stannichloride. EDWARD BARNES (*Chem. News*, 1919, **119**, 13—14).—In the course of the reduction of azobenzene to benzidine by boiling with stannous chloride in hydrochloric acid, a benzidine stannichloride having the composition

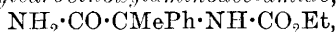


was isolated. The salt forms colourless needles, which are stable in dry air at the ordinary temperature, but evolve hydrochloric acid and stannic chloride when heated to 100°. It is considerably hydrolysed by water or dilute hydrochloric acid, and is only deposited from solution in presence of a large excess of stannic chloride. When mercuric chloride is added to a solution of the benzidine stannichloride, a mercuric salt is precipitated. The composition of the precipitate is indefinite, but by mixing hot solutions of mercuric chloride and benzidine hydrochloride in

equivalent proportions, the salt, $C_{12}H_8(NH_2)_2 \cdot 2HCl \cdot HgCl_2$, is obtained, crystallising in transparent blades, slightly soluble in cold dilute hydrochloric acid, readily in hot. E. H. R.

Preparation of Hydantoins. CHEMISCHE FABRIK VON HEYDEN (D.R.-P. 310427, additional to D.R.-P. 309508 and 310426; from *Chem. Zentr.*, 1919, ii, 423—424. Compare this vol., i, 351).—Substances of the types $NH_2 \cdot CO \cdot NH \cdot CRR' \cdot CO_2H$,

$CO_2H \cdot NH \cdot CRR' \cdot CO \cdot NH_2$, and $NH_2 \cdot CRR' \cdot CO \cdot NH \cdot CO_2H$ (R =alkyl, R' =aryl or alkyl, with the exception of methyl or ethyl) are treated with a condensing agent, or condensation is effected without an agent by warming in the presence or absence of a solvent or diluent. The saporifics of the main patent are obtained in this manner. *CC*-Dipropylhydantonitrile, $CN \cdot CPr_2 \cdot NH \cdot CO \cdot NH_2$, colourless needles, m. p. 138° , is obtained by converting dipropylketocyanohydrin by means of ammonia into the amino-nitrile, and treating the latter with potassium cyanate in hydrochloric acid solution. It is converted by boiling concentrated hydrochloric acid into *CC*-dipropylhydantoin. A solution of phenylmethylaminoacetoneitrile in hydrochloric acid is converted by potassium cyanate into *phenylmethylhydantonitrile*, colourless needles, m. p. 217° (decomp.), which is further transformed into *phenylmethylhydantoin*, small needles, m. p. 197° . Ethyl *CC*-phenylmethylhydantoate, colourless needles, m. p. 158° , is obtained from ethyl α -amino- α -phenylpropionate hydrochloride and potassium cyanate, and yields *CC*-phenylmethylhydantoin by prolonged boiling with water or by heating alone at 200° . The same substance may also be prepared by the action of potassium hydroxide solution (33%) on *CC*-phenylmethylcarbethoxylaminoacetamide,

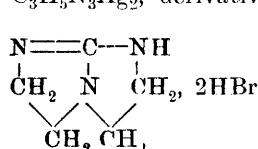


colourless needles, m. p. 191° (from α -amino- α -phenylpropionamide and methyl chloroformate in the presence of sodium carbonate). *CC*-Phenylethylhydantoin is obtained by the action of carbonyl chloride in benzene solution on phenylethylaminoacetamide; carbonyl chloride may be replaced by oxalyl chloride. *CC*-Phenylmethylthiohydantoin, $\begin{matrix} Ph \\ | \\ M > C < \begin{matrix} CO-NH \\ | \\ NH-CS \end{matrix} \end{matrix}$, colourless needles, m. p.

169° , is prepared by boiling an alcoholic solution of phenylmethylaminoacetamide with carbon disulphide; if the thiohydantoin is dissolved in boiling sodium hydroxide solution (40%) and the solution diluted with water and again boiled after addition of ferrous sulphate, *CC*-phenylmethylhydantoin is produced. H. W.

Ethyleneguanidine and Diethyleneguanidine. P. PIERRON (*Ann. Chim.*, 1919, [ix], 11, 361—368).—Ethylenediamine in 10% solution and cyanogen bromide, when mixed in equimolecular proportions, readily react to give *ethyleneguanidine hydrobromide*, $\begin{matrix} CH_2-NH \\ | \\ CH_2-NH \end{matrix} > C:NH, HBr$, m. p. 125 — 126° . From this, by suitable

double decomposition, the *sulphate*, $(\text{C}_3\text{H}_7\text{N}_3)_2\text{H}_2\text{SO}_4$, m. p. 281° , the *nitrate*, $\text{C}_3\text{H}_7\text{N}_3\cdot\text{HNO}_3$, m. p. 115° , and the *hydrochloride*, m. p. $120\text{--}122^\circ$, were obtained. Attempts to isolate the base itself were not successful, but from its aqueous solution, by the action of carbon dioxide, the *carbonate*, $(\text{C}_3\text{H}_7\text{N}_3)_2\text{H}_2\text{CO}_3$, m. p. 162° , was obtained. Ethyleneguanidine gives metallic derivatives, the *barium*, $\text{C}_3\text{H}_5\text{N}_3\text{Ba}$, *lead*, $\text{C}_3\text{H}_5\text{N}_3\text{Pb}$, *silver*, $\text{C}_3\text{H}_6\text{N}_3\text{Ag}$, and *disilver*, $\text{C}_3\text{H}_5\text{N}_3\text{Ag}_2$, derivatives being prepared.



If ethylenediamine is mixed with cyanogen bromide in the molecular proportion of 2:1, or, better still, if ethyleneguanidine hydrobromide is evaporated with an equimolecular proportion of ethylenediamine, *diethyleneguanidine dihydrobromide* (annexed formula), m. p. 224° , is obtained. From this, the *dipicrate*, $\text{C}_5\text{H}_9\text{N}_3\cdot 2\text{C}_6\text{H}_3\text{O}_7\text{N}_3$, m. p. 203° , and the *dinitrate*, $\text{C}_5\text{H}_9\text{N}_3\cdot 2\text{HNO}_3$, m. p. 138° , may be prepared. W. G.

Amphoteric Colloids. V. The Influence of the Valency of Anions on the Physical Properties of Gelatin. JACQUES LOEB (*J. Gen. Physiol.*, 1919, 1, 559—580).—The author has previously suggested a tentative theory to explain the fact that whilst gelatin salts with a univalent cation show a high degree of swelling, viscosity, osmotic pressure, and alcohol number, and gelatin salts with a bivalent metal show, for the same p_{H} and concentration of gelatin a low degree of swelling, viscosity, osmotic pressure, and alcohol number, yet the conductivities of the two types of salts are practically the same (this vol., i, 296). Curves representing the influence of monobasic acids (hydrochloric, hydrobromic, nitric, and acetic acids) on the osmotic pressure, swelling, and viscosity of gelatin solutions are practically identical, whereas those representing the effect of sulphuric acid are much lower, and stand very much in the same relation to the curves of the monobasic acids as do the curves for calcium gelatin to those for sodium gelatin.

The curves representing the influence of other dibasic acids, namely, oxalic, tartaric, succinic, citric, and phosphoric acids, are practically identical with those of the monobasic acids. If the author's theory is correct and it is true that the effect of an electrolyte on the physical properties of the colloid is due to the formation of real chemical compounds between the colloid and one of the ions of the electrolyte, it should be possible to prove, first, that twice as many molecules of hydrobromic acid as of sulphuric acid combine with a given mass of gelatin, and secondly, that the same number of molecules of phosphoric, citric, tartaric, oxalic, or succinic acid combine with the same mass of gelatin as of nitric or hydrochloric acid. The present paper gives experimental proof that both these conditions hold.

Gelatin sulphate and gelatin bromide solutions possessing the same p_{H} have practically the same conductivity. Hence the difference in effect of sulphates and bromides on the physical properties

of gelatin cannot be due to the different ionising and hydration effects of the two acids on the protein molecule. J. C. D.

Pekelharing's Pepsin. V. The Inhibition of the Action of Pepsin by the Bile Acids. W. E. RINGER (*Arch. Néerland. Physiol.*, 1919, **3**, 349—360).—The bile acids inhibit the proteolytic action of pepsin. This is not due to a destruction of the enzyme, for if the bile acids are removed by dialysis the proteolytic activity of the pepsin is restored to its original value. The inactivation is probably a result of adsorption phenomena, and the action of the bile acids closely resembles that of certain ions such as the ferrocyanide ion. J. C. D.

Physiological Chemistry.

The Presence of Phosphates in Human Blood-serum. VIII. The Partition of Phosphorus, with Especial Reference to the Phosphorus in Combination with Proteins. JOH. FEIGL (*Biochem. Zeitsch.*, 1919, **94**, 293—303. Compare A., 1918, i, 50, 203, 320, 357; this vol., i, 138).—A further study of the distribution of phosphorus in human blood in normal and pathological cases.
J. C. D.

The Presence of Phosphate in Human Blood-serum. IX. A Study of Methods and the Distribution of Phosphorus in Normal Erythrocytes. JOH. FEIGL (*Biochem. Zeitsch.*, 1919, **94**, 304—312).—The methods and technique are discussed, and figures representing the distribution of phosphorus in the normal red blood cells are given.
J. C. D.

Physical Scheme for the Study of the Mineral Nutrition of the Cell. PIERRE GIRARD (*Compt. rend.*, 1919, **168**, 1335—1338).—Working on the lines of his previous experiments (compare A., 1908, ii, 456; 1909, ii, 463), the author shows that, in the case of a solution of barium chloride, the barium and chlorine ions will diffuse through a membrane into water, at different proportional rates, according as the solution is acidified with a trace of nitric acid or made alkaline with a trace of ammonia, polarisation occurring at the membrane. These experiments are quoted in further support of his views on the selective permeability of living membranes (*loc. cit.*).
W. G.

Enzyme Studies on Cellulose Degradation Products. HANS PRINGSHEIM and ADELHEID MAGNUS VON MARKATZ (*Zeitsch. physiol. Chem.*, 1919, **105**, 173—178).—The authors have prepared a cellulose dextrin free from products yielding an osazone reaction

by the method of Madsen (Inaug. Diss., 1917). No evidence of this substance being degraded by the action of diastase could be obtained, nor did emulsin, by virtue of its cellobiase, bring about the formation of any products yielding osazones. Extracts of the first stomach, small intestine, and pancreas of oxen, likewise, had no hydrolytic action, so the conclusion is reached that in the intestinal tract of these animals cellobiose is split by the action of bacteria. Cellobiose is not oxidised to cellobionic acid on boiling with yellow mercuric oxide. J. C. D.

The Stability of Lactalbumin towards Heat. A. D. EMMETT and G. O. LUROS (*J. Biol. Chem.*, 1919, **38**, 257—265).—The biological value of lactalbumin as a protein for growth did not appear to be diminished by heating at 90—100° in an air oven for sixteen hours, or by treatment in an autoclave at fifteen pounds pressure for two or six hours. There was certainly no evidence that the heated protein was toxic for young rats. The previous conclusions regarding the excellent growth-promoting value of lactalbumin (this vol., i, 363) is further substantiated on the hypothesis that there is a vitamine factor involved which is different from the so-called water-soluble B. J. C. D.

The Nutritive Value of Yeast Protein. THOMAS B. OSBORNE and LAFAYETTE B. MENDEL (*J. Biol. Chem.*, 1919, **38**, 223—227).—Rats were kept for more than a year, covering the period of growth, on a diet in which yeast furnished the sole source of nitrogen, as well as of the water-soluble vitamine. The animals showed a normal rate of growth, but certain cases exhibited sterility on arriving at maturity. This is not attributed to the presence of a toxic factor in the yeast. J. C. D.

The Zinc Content of some Food Products. VICTOR BIRCKNER (*J. Biol. Chem.*, 1919, **38**, 191—203).—The author found the method proposed by Breyer (Scott, "Standard Methods of Chemical Analysis," 1917, 487) satisfactory for the estimation of very small quantities of zinc. Hen's eggs contain about 1 mg. of zinc, of which practically all is present in the yolk. Ordinary market milk contains on an average 4.2 mg. of zinc per kilo, but variations are to be found in the milk from different animals. The zinc content of human milk is markedly higher than that of cow's milk. The presence of zinc both in egg yolk and in milk suggests that this element may exert an important function in nutrition. J. C. D.

The Degradation of Fatty Substances in the Central Nervous System. ELSE HIRSCHBERG and HANS WINTERSTEIN (*Zeitsch. physiol. Chem.*, 1919, **105**, 1—19).—The amount of alkali bound after boiling the spinal cord of the frog with *N*/10-sodium hydroxide for two hours may be taken as a measure of the amount of fatty substances present. Using this method of estimation, the authors have shown that the fat content of the surviving cord

gradually diminishes when it is kept in an atmosphere of oxygen or in oxygenated physiological saline solution. The decrease is due to oxidation processes, and is more marked when stimulation is applied. Considerable fat-sparing action may be shown by certain carbohydrates; thus, dextrose may reduce the utilisation of fatty substances some 40% in resting metabolism, and as much as 80% in stimulation. Reasons are given for believing that the substances which bind alkali on hydrolysis, and are utilised during oxidation, are of the nature of phosphatides rather than of true fats.

J. C. D.

The Protein Sugar. HENRI BIERRY (*Compt. rend.*, 1918, 168, 1225—1228. Compare Bierry and Fandard, A., 1914, i, 218, 454, and Bierry and Ranc, A., 1914, i, 346).—If the muscle plays a part in the genesis of protein sugar, differences in the protein sugar content should be found between the arterial plasma and venous plasma from the same group of muscles. This has been shown to be true for the group of muscles of the thigh in the case of the dog. The author suggests that in the muscular protoplasm there exists a complex nitrogenous molecule, the nucleus of which remains invariable, but has attached to its terminal chains peptidic groupings capable of being liberated and then regenerated. These groupings can unite with dextrose and block its aldehyde function.

W. G.

Colours of Colloids. VI. Blue Eyes. WILDER D. BANCROFT (*J. Physical Chem.*, 1919, 23, 356—361. Compare this vol., ii, 275, 324).—In the present paper the colour of blue eyes is discussed. It is shown that there is no pigment on the front of the iris in blue eyes, the blue colour is due to turbid media and is richer the finer the suspended particles. When the uvea is lacking, the colour of the blood shows through and albinism is the result. All other colours in eyes are due to pigmentation on the front of the eye, which either modifies or masks the blue of the turbid media.

J. F. S.

Zinc in Oysters. R. S. HILTNER and H. J. WICHMANN (*J. Biol. Chem.*, 1919, 38, 205—221).—Zinc was invariably found present in the oysters, all of which were grown in Atlantic waters. It is probable that copper is always associated with the zinc. The amount of zinc found could not be correlated with the weight of the system or with the zinc content of the water in which they grew. Considerable quantities of zinc and sometimes traces of copper were detected in the vegetation and organic matter dredged up with the oysters.

It appears probable that zinc and copper can be absorbed by the tissues of the oysters in quantities far in excess of functional requirements.

J. C. D.

Pyrrole and Melanuria. PIETRO SACCARDI (*Atti R. Accad. Lincei*, 1919, [v], 28, i, 309—311).—Subcutaneous administration

of pyrrole to a rabbit produces a green coloration of the urine, which afterwards becomes brown. Such urine exhibits no pathological characters, retains its normal alkalinity, and responds to the reactions regarded as characteristic of the melanogens. T. H. P.

Hæmatoporphyrin Congenita. II. O. SCHUMM (*Zeitsch. physiol. Chem.*, 1919, **105**, 158—172).—The daily excretion of crude porphyrin in the urine in cases of this disease was found to be fairly constant at various periods during two years. Analyses of crude porphyrin from urine gave higher values for carbon and lower values for hydrogen and nitrogen than were recorded by Fischer (A., 1916, i, 514). The figures for nitrogen are markedly higher than the nitrogen content of free urinoporphyrin, so that it is probable that the crude product is a chemical or physical complex of the pigment with a substance rich in nitrogen. Analyses of purified porphyrin-methyl ester from urine agree with the formula deduced by Fischer, $C_{47}H_{50}O_{16}N_4$. Analyses of the porphyrin methyl ester from fæces agree with Fischer's formula, $C_{39}H_{42}O_8N_4$. The author confirms his previous observation of the occurrence of porphyrin and hæmatin in the blood of patients with this disease, and now finds considerable amounts of bilirubin also. J. C. D.

New Theory relating Constitution to Taste. Simple Relations between the Constitution of Aliphatic Compounds and their Sweet Taste. ERNEST OERTLY and ROLLIN G. MYERS (*J. Amer. Chem. Soc.*, 1919, **41**, 855—867).—A preliminary paper, in which a theory of the cause of the taste of sweet substances is put forward. The taste of sweet substances depends on two factors, the presence of a glucophore and an auxogluc. An auxogluc is an atom or radicle which, combined with any glucophore, yields a sweet compound. A glucophore is a group of atoms which has the power to form sweet compounds by uniting with a number of otherwise tasteless atoms or radicles. This theory is considered in the present paper only in connexion with aliphatic compounds. In the sense of the theory the following radicles are glucophores:

(1) $-\text{CO}\cdot\text{CH}(\text{OH})-(+\text{H})$;

(2) $\text{CO}_2\text{H}\cdot\text{CH}(\text{NH}_2)-$; (3) $-\text{CH}_2\cdot\text{O}\cdot\text{NO}_2$; (4) $\text{CH}_2(\text{OH})\cdot\text{CH}(\text{OH})-$;

(5) $\text{C}_{\text{Hal}}^{\text{H}_2-x}$; (6) $\text{C}_{\text{Hal}}^{\text{H}_2-x}\cdot\text{C}_{\text{Hal}}^{\text{H}_2-y}$. The following atoms or radicles act as

auxoglucs, forming sweetish compounds with glucophores: (a) hydrogen, (b) the radicles $\text{C}_n\text{H}_{2n+1}$, containing 1—3 carbon atoms, (c) the radicles $\text{C}_n\text{H}_{2n+1}\cdot\text{O}-$, of the monohydric alcohols, where $n=1$ or 2, (d) the radicles $\text{C}_n\text{H}_{2n-1}\text{O}_n$ of the polyhydric alcohols. A very long list of sweet substances supporting this theory is given. The presence of the phenyl group tends to make an otherwise sweet compound bitter. Thus ethylene glycol is sweet, but its phenyl derivative is slightly bitter. Some exceptions to the rule are found in stereoisomeric substances; thus *l*-valine, $\text{CHMe}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$, is made up of the glucophore,

$-\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$,

and the auxogluc, CHMe_2 -, and is slightly bitter, but *d*-valine and *dl*-valine are both sweet.

J. F. S.

Is there a Relationship between the Power of Absorbing Radiant Heat and the Odour of Substances? G. GRIJNS (*Arch. Néerl. Physiol.*, 1919, **3**, 377—390).—The various attempts which have been made to trace a relationship between the odour of substances and their chemical constitution or physical properties are reviewed. Tyndall ("Heat as a Mode of Motion," London, 1865, 366) observed that gases with an odour possessed the power of absorbing radiant heat to a marked degree. The author has attempted to study this point more fully and quantitatively. An apparatus, termed an odorimeter, devised by Prof. Zwaardemaker for the quantitative measurement of odours is described. No relation between the intensity of the odour and the power of absorbing radiant heat is detected, and it is therefore concluded that the stimulation of the olfactory apparatus is not effected by the liberation of energy absorbed from radiant heat.

J. C. D.

The Biological Action of Thorium. H. JASTROWITZ (*Biochem. Zeitsch.*, 1919, **94**, 313—358).—No demonstrable influence of thorium on nuclease or uricolysis was observed. After injections of thorium into dogs, there was a tendency for a higher excretion of uric acid than normally. The fact that thorium may delay the separation of uric acid from its supersaturated solution in serum is held to be of importance from a clinical point of view. The peptolytic enzymes are not influenced by thorium, but the peroxylase is inhibited.

J. C. D.

Genesis of Thiocyanic Acid in Animals. VI. SERAFINO DEZANI (*Arch. Farm. sperim. sci. aff.*, 1918, **26**, 115—128; from *Chem. Zentr.*, 1919, i, 485—486. Compare this vol., i, 138).—It has been shown by Bruylants that carbon disulphide is converted into thiocyanic acid by the animal organism. Thiocarbamide appears to be a possible intermediate compound, since its presence in the organism has been detected by Gautrelet. In the case of the rabbit, administration of thiocarbamide did not lead to an increase in the thiocyanic acid in the urine. In the cases of both the rabbit and the dog, elimination of the acid depends greatly on the nature of the nourishment. It is very small when clover is given, but very marked with cauliflower. Its origin with the rabbit is exogenic in nature.

H. W.

Effect of Various Aromatic Substances on the Blood Vessels. Comparison of the Constitution and Action of Drugs. S. KONDO (*Kyoto Igaku Zasshi*, 1917, **14**, No. 7, 25—75; *Jap. Med. Literature*, 1919, **4**, 18).—The compounds studied were vasodilators, similar in action but differing in degree. They stimulated first the nerve, then the muscle fibre, and vascular paralysis was produced. With few exceptions, if the vasodilator was given

sufficient time to act, the vasoconstrictor action of barium and of adrenaline was prevented. The physiological action of compounds of the aromatic series is due to the benzene nucleus, and is modified by substituents. Monohydric phenols had a more powerful action than either benzene or dihydric or trihydric phenols; a similar relation existed between sodium benzoate and salicylate, and between *cyclohexanol* and quinitol (*cyclohexane-1:4-diol*). Of the three isomeric dihydroxybenzenes, resorcinol exerted the greatest vasodilator action. Guaiacol was more powerful than catechol, phenacetin than antifebrin, lactophenine than aniline, phenylhydrazine than aniline. The toxicity was increased by the union of two nuclei. Naphthalene was more toxic than benzene, benzidine than aniline, and quinoline than pyridine. Menthol and camphor had an identical action; pyridine and nicotine acted similarly, likewise quinoline and quinine. *cycloHexane* was more powerful than benzene, and piperidine than pyridine. *cycloHexanol* did not exert a more marked action than phenol.

CHEMICAL ABSTRACTS.

Chemistry of Vegetable Physiology and Agriculture.

Biochemical Action of Microbes on³Sugars and Alcohols.

A. BESSON, A. RANQUE, and CH. SENEZ (*Compt. rend. soc. biol.*, 1918, **81**, 930—933; from *Chem. Zentr.*, 1919, i, 663—664).—A table is given showing the action of various microbes (*Bacillus faecalis alkaligenes*, *B. pyocyaneus*, *B. Shiga*, *B. Hiss*, *B. Flexner*, *B. typhi*, *Vibrio cholerae*, *B. proteus*, *B. paratyphi A*, *B. paratyphi B.*, *B. coli*) on dextrose, lævulose, maltose, dulcitol, sucrose, lactose, mannitol, and glycerol in the presence of agar or peptone water. The mode of action depends greatly on the form of nutriment, and the manner in which the different sugars and alcohols are attacked does not depend on the nature of the substances, but is a specific property of the respective microbes. The evolution of gas seems to be a more important phenomenon than the fact that a particular sugar is or is not attacked. With regard to their action on sugars and alcohols, microbes may be conveniently classified as follows: (i) inactive microbes which do not attack these substances; (ii) microbes which act without evolving gas; (iii) such as act with evolution of gas. The latter two groups may be subdivided according to the susceptible individual compounds.

H. W.

Benzoic Acid as a Disinfectant. H. P. KAUFMANN (*Zeitsch. angew. Chem.*, 1919, **32**, 199—200).—The bactericidal action of benzoic acid on bouillon cultures of *Staphylococcus* and diphtheria bacilli was investigated, and concentrations as low as 0.08% in the former case and 0.04% in the latter were found to produce

sterility in five days. In steam or water vapour at temperatures as low as 37°, benzoic acid showed a powerful bactericidal action comparable with that of phenol under similar conditions. The volatility of benzoic acid in water vapour from boiling aqueous solutions was determined by passing the vapours through a condenser and estimating the benzoic acid in the distillate. With 1% solutions, the percentage gradually increased from 0.256 at the commencement to 1.088 when 90% of the solution had been distilled off, at which point the remaining acid began to separate as an oil. With 2.5% solutions, the benzoic acid content of the distillate rose from 0.605% initially to 1.006% when 70% had distilled and oil began to separate. With 5% solutions, the corresponding figures were 0.995%, rising to 1.06% when 30% had distilled over. [See, further, *J. Soc. Chem. Ind.*, 1919, August.] G. F. M.

Increase of the Action of Catalase in Yeast Cells. HANS VON EULER and RAGNAR BLIX (*Zeitsch. physiol. Chem.*, 1919, 105, 83—114).—The researches of Phragmén (*Medd. K. Vetenskaps-akad. Nobel-Inst.*, 1919, 5) have shown that fresh yeast can bring about the decomposition of dilute hydrogen peroxide. The decomposition follows, within certain limits, the course of a unimolecular reaction. The reaction constant increases proportionately to the amount of yeast used. The power of decomposing hydrogen peroxide possessed by the living yeast may be increased from two to six times by the addition of small quantities of protoplasmic poisons, such as chloroform, thymol, toluene, and phenol. Analogous cases have been described (Euler and Johansson, A., 1912, i, 807). The catalase action of yeast is also greatly increased by drying at the ordinary temperature, or by dehydration by other means—treatment with alcohol or acetone—provided the enzyme is not destroyed. No appreciable increase in the catalase action of the dried yeast was observed to follow the addition of chloroform or toluene. When emulsions of fresh yeast are maintained at 55—63° for from one-half to two hours, there is also a very great increase in the power of decomposing hydrogen peroxide. Such activation is not confined to yeast, but is also found in the case of numerous other organisms.

The catalase action per cell may be raised by treating the yeast with nutritive solutions containing sucrose. The influence of a reducing agent, such as methylene-blue, is to cause an increased activation of catalase, whereas acetaldehyde has an inhibitory action.

The influence of dehydration and of protoplasmic poisons on the enzymes of yeast is discussed, and it is considered not improbable that in the case of catalase they act by preventing or neutralising the action of an inhibitory factor. J. C. D.

Antagonism between Alkaloids and Salts in Relation to Permeability. W. J. V. OSTERHOUT (*J. Gen. Physiol.*, 1919, 1, 515—519).—It was found that nicotine, caffeine, and cevadine may

antagonise the action of sodium chloride. They decrease permeability, and resemble in this respect salts, such as calcium chloride, which antagonise sodium chloride. J. C. D.

Two Crystalline Salts from the Phospho-organic Reserve Principle of Green Plants. S. POSTERNAK (*Compt. rend.*, 1919, 168, 1216—1219. Compare A., 1903, ii, 607, 679, 680).—The author describes methods for preparing two crystalline phospho-organic salts from seeds or from phytin. The first salt is a double sodium calcium salt having the composition $C_6H_{12}O_{27}P_6Ca_2Na_8$, and crystallising in slender needles. The second is a sodium salt, $(C_2H_4O_9P_2Na_4)_3 \cdot 44H_2O$. It crystallises in prisms, and readily yields the corresponding copper and lead salts. W. G.

The Constitution of the Phospho-organic Reserve Principle of Green Plants. S. POSTERNAK (*Compt. rend.*, 1919, 169, 37—39. Compare preceding abstract).—The author now inclines to the view that this material is an inositol hexaphosphate which energetically retains 3 mols. of water, and these cannot be removed without decomposing the compound. W. G.

Studies on Enzyme Action. XVII. The Oxydase, Peroxydase, Catalase, and Amylase of Fresh and Dehydrated Vegetables. K. GEORGE FALK, GRACE MCGUIRE, and EUGENIA BLOUNT (*J. Biol. Chem.*, 1919, 38, 229—244).—The oxydase reactions with carrot, yellow or white turnip, potato, and tomato juices are greatly increased on dilution. Apparently some substance, chemically unsaturated, is present which combines with the oxygen, preventing it from acting on the reagent. The peroxydase reaction did not show such increase on dilution. There is no well-defined hydrogen-ion concentration for the maximum action with oxydase, peroxydase, or catalase, but the reactions are, in general, better between $p_H 7$ and $p_H 10$. They are inhibited by acid reaction, except in the case of the tomato. Vacuum dehydrated cabbage and carrot gave more marked oxydase reactions than did the fresh vegetables, but in every other case the enzyme action was less after dehydration. Well-defined maxima in the amylase reactions are apparent in cabbage, carrot, and turnip juices at about $p_H 6$. Dehydration causes a decrease in the activity of this enzyme. J. C. D.

A Component of the Fat of *Bassia longifolia* L. (Illipe Malabrorum Kön) and *Bassia latifolia*. E. WINTERSTEIN (*Zeitsch. physiol. Chem.*, 1919, 105, 31—32).—On preserving pieces of the press cake of seeds of *Bassia longifolia* and *B. latifolia* in an evacuated vessel over phosphoric oxide for several months at 30—35°, the surface of the cake became covered with fine, needle-shaped crystals. These were identified as palmitic acid. J. C. D.

The Resin of the Outer Bark of *Melaleuca uncinata*. HENRY G. SMITH (*J. Proc. Roy. Soc. N.S. Wales*, 1917, 51, 232—237).—The thin, paper-like epidermis of the stems and

branches of *Melaleuca uncinata* contains from 20—25% of a resin, which can be extracted with hot alcohol. The resin resembles ordinary shellac in appearance and has D_{15}^{20} 1.135. About 70% of the total resin is an acid resin, m. p. 148—150°, which gives a *potassium* and a *silver* salt. The neutral substances constitute about 25% of the original resin.

In addition to the resin, the outer bark contains a small amount of a vegetable wax, m. p. 67—68°. W. G.

Isolation of a Saponin from *Platycodon grandiflorum* Root. H. OSHIKA (*Kyoto Igaku Zasshi*, 1918, 15, No. 2, 76—83; *Jap. Med. Literature*, 1919, 4, 20).—The root of the herbaceous plant *Platycodon grandiflorum* (Japanese “Kikyo,” Chinese “Kihkang” or “Kihung”) is used as an astringent, carminative, sedative, and vermifuge. It contains a *saponin*, which has the formula $C_{35}H_{48}O_{20}$, is a white powder when pure, is sparingly soluble in water, more readily so in alkali, and is insoluble in acids, ether, and chloroform. Its hæmolytic power is approximately one half that of dioscin. The infusion or decoction of the root has a toxicity for the mouse approximately equal to that of senega root.

CHEMICAL ABSTRACTS.

Composition of Inclusion Cells and their Relation to the Mellowing of Fruits. C. GRIEBEL and A. SCHÄFER (*Zeitsch. Nahr. Genussm.*, 1919, 37, 97—111).—The mesocarp of certain fruits (especially the *Pyrus* species) consists solely of cells containing tannins, and the term “inclusion” cells is given to them, as a distinction from the tannin idioblasts of other fruits and plants. When ripe, fruits having such a mesocarp rapidly become over-ripe or mellow. The single exception, as regards mellowing, is the fruit of *Prunus spinosa* (sloe). The disappearance of the astringent taste during mellowing is not due to decomposition of the tannins, but to their becoming insoluble. The inclusion cells of *Pyrus domestica* contain a tannin which is soluble in water and alcohol; this tannin is, in part, combined with a sparingly soluble colloidal substance of unknown composition; only when the fruit mellows or is dried do the cell contents become insoluble, brown-coloured substances being formed gradually as this change takes place. Acetaldehyde is formed during the mellowing. The quantity of pentosan and galactan in the inclusion cells of *P. domestica* is very small, and sugars do not appear to be present. The unchanged tannin in the cells yields the reactions of *o*-hydroxy-compounds, an indication that it is a catechol derivative; fusion with potassium hydroxide yields a small quantity of protocatechuic acid, but no phloroglucinol. The tannin possesses no glucosidal character, and its properties resemble those of the oak-bark tannins. W. P. S.

The Presence of Aconitic Acid in Sugar-cane Juice and a New Reaction for the Detection of the Acid. CHARLES SOMERS TAYLOR (T., 1919, 115, 886—889).

Effect of Manganese Compounds on Soils and Plants.

E. P. DEATRICK (*Cornell Univ. Agric. Exp. Sta. Mem.*, 1919, **19**, 371—402).—Manganese salts at high concentrations decrease the growth of wheat in water cultures; at lower concentrations, they stimulate the growth of the plants and increase the oxidising power of the roots. The presence of nutrient salts and the food stored in the endosperm of the wheat seed reduce the toxic effect of the manganese salts. The toxic effect is shown by a browning of the roots and a bleaching of the leaves. The bleached leaves of plants treated with manganese salts contain more manganese than the green leaves. Manganese salts added to the soil increase the power of the soil to oxidise aloin and phenolphthalein. This the author believes is due to the formation of manganese dioxide. Low concentrations of manganese salts stimulate the ammonification of dried blood, but inhibit the nitrification of ammonium sulphate in the soil.

CHEMICAL ABSTRACTS.

Acidimetric Titration of Grain Extracts and Amino-acids in the Presence of Alcohol.

VICTOR BIRCKNER (*J. Biol. Chem.*, 1919, **38**, 245—254).—It was found that a larger amount of alkali is required to neutralise the acidity of grain extracts when alcohol is present. A study of this point showed that amino-acids, which in aqueous solution are nearly neutral to phenolphthalein, react distinctly acid in the presence of alcohol. The suggestion is advanced that this may be due to an interaction between the hydrated form of the amino-acid and the alcohol. J. C. D.

Constituents of Emmenthaler Cheese.

V. E. WINTERSTEIN (*Zeitsch. physiol. Chem.*, 1919, **105**, 25—30. Compare A., 1902, ii, 687; 1904, ii, 585; 1906, ii, 248; 1909, ii, 423).—It has been previously shown that the usual protein cleavage products can be isolated from this cheese, with the one exception of arginine. Arginine was not present in several kinds of skimmed-milk cheese examined. The fate of the arginine has been inquired into. This amino-acid might by ferment action give rise to agmatine, 1:4-diaminobutane, ornithine, urea, and ammonia. 1:4-Diaminobutane was not present, but the presence of urea and ornithine was established. Traces of *p*-hydroxyphenylethylamine were also detected. J. C. D.

The Statement of Acidity and Alkalinity, with Special Reference to Soils.

EDGAR T. WHERRY (*J. Washington Acad. Sci.*, 1919, **9**, 305—309).—The author proposes a new method of expressing acidity or alkalinity in place of the usual potential method, in which the value $P_H=7$ indicates neutrality. His scale for chemical potentials is such that $X_H=0$ indicates neutrality, acidity being expressed by positive values and alkalinity by negative. These new values may be arrived at by subtracting the values of P_H from 7. W. G.

Organic Chemistry.

The Preparation of some True Acetylenic Hydrocarbons by means of Monosodioacetylene. PICON (*Compt. rend.*, 1919, **169**, 32—34. Compare this vol., i, 246).—Normal amyl iodide reacts with monosodioacetylene in liquid ammonia, yielding heptinene, together with a small amount of β -methyl- Δ^1 -butene, the latter due probably to the presence of a small amount of active amyl iodide in the sample used.

Normal primary octyl iodide in the same way yields *aecinene*, b. p. $59^\circ/13$ mm., m. p. -40° , D_4^{20} 0.791, and hexadecyl iodide gives octadecinene, m. p. 22.5° , D_4^{20} 0.8696. W. G.

Carbon Tetrachloride, Chloroform, and Carbon Hexachloride from Natural Gas. G. W. JONES and V. C. ALLISON (*J. Ind. Eng. Chem.*, 1919, **11**, 639—643).—Natural gas rich in methane or ethane, such as that of Pittsburgh, can be used for the production of carbon tetrachloride, chloroform, and carbon hexachloride. For this purpose, it is passed, together with a slight excess of chlorine, through a tube which contains a suitable catalyst, and is heated in an electric furnace. The most suitable catalysts are war-gas charcoal, "bachite" (a patent carbon material), and steamed anthracite coal, all of which have a high absorptive capacity for chlorine. The reaction begins at 250° and increases in intensity up to about 500° , above which the catalyst is attacked and carbon is deposited. One litre of natural gas (90% of methane and 10% of ethane) when completely chlorinated should yield 4.01 c.c. of chlorination products. Methane is less readily chlorinated than higher saturated hydrocarbons. By introducing the gas at the rate of 1 litre per hour, methane is completely converted into carbon tetrachloride and ethane into carbon hexachloride. By increasing the rate of introduction of the natural gas, chloroform is obtained in addition to carbon tetrachloride. [See also *J. Soc. Chem. Ind.*, 1919, 599A.] C. A. M.

Preparation of Tetrachloroethylene. H. B. WEISER and G. E. WIGHTMAN (*J. Phys. Chem.*, 1919, **23**, 415—439).—The optimum temperature for the thermal decomposition of carbon tetrachloride into chlorine and tetrachloroethylene lies between 1300° and 1400° , but a certain amount of decomposition occurs at temperatures as low as 600° . In order to minimise the further reaction of chlorine on tetrachloroethylene to form solid hexachloroethane, the products of decomposition must be cooled as rapidly as possible, and may with advantage be diluted with an inert gas such as air or nitrogen. The decomposition is conveniently conducted in an electrically heated quartz tube, and an iron condenser may be used provided that the condensing surface

is kept dry and comparatively cool. [See also *J. Soc. Chem. Ind.*, 1919, September.] G. F. M.

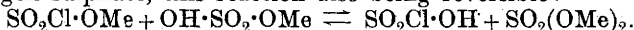
The Catalytic Formation of Alkyl Chlorides from Primary Alcohols. PAUL SABATIER and A. MAILHE (*Compt. rend.*, 1919, 169, 122—125).—When the vapours of primary alcohols of the methyl series are passed along with hydrogen chloride over aluminium oxide at 420°, the corresponding primary alkyl chloride, together with some secondary or tertiary chloride and some ethylenic hydrocarbon, is obtained. In this way, propyl alcohol gives a mixture of propyl and *isopropyl* chlorides, the latter predominating; *isobutyl* alcohol gives a mixture of *isobutyl* chloride, $\text{CHMe}_2\cdot\text{CH}_2\text{Cl}$, and the tertiary chloride, CMe_3Cl , in the proportion of 1:3; *isoamyl* alcohol gives a mixture of the primary, secondary, and tertiary chlorides in the proportion of 1:2:3, and heptyl alcohol gives heptene and a mixture of primary and secondary heptyl chlorides, together with a little diheptene.

W. G.

The Spontaneous Oxidation of Organic Complexes of Cobalt. H. COLIN and O. LIÉVIN (*Compt. rend.*, 1919, 169, 188—190).—Alkaline solutions of certain organic substances in the presence of cobalt sulphate undergo spontaneous oxidation in the air. In some cases, the amount of oxidation is limited, whilst in others it increases with the time. Glycerol and lactic acid furnish examples of the first type, whilst dextrose, mannitol, erythritol, and tartaric acid are examples of the second class of organic substances. As explanation of this phenomenon, the authors suggest that the cobalt, in the presence of alkali, forms true complexes with the organic compounds. These complexes oxidise spontaneously and turn green, the organic substance being attacked at the same time. If the products of this secondary oxidation are capable of reducing the green complex, there is a continuous transportation of oxygen, but if not the absorption is limited.

W. G.

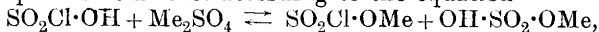
Action of Chlorosulphonic Acid on Methyl Hydrogen Sulphate. R. LEVAILLANT and L.-J. SIMON (*Compt. rend.*, 1919, 169, 140—143).—Methyl hydrogen sulphate reacts with chlorosulphonic acid to give methyl chlorosulphonate according to the equation $\text{OH}\cdot\text{SO}_2\text{Cl} + \text{OH}\cdot\text{SO}_2\cdot\text{OMe} \rightleftharpoons \text{SO}_2\text{Cl}\cdot\text{OMe} + \text{H}_2\text{SO}_4$. This reaction is, however, reversible, and an equilibrium is set up. At the same time, a secondary reaction proceeds between some of the methyl chlorosulphonate formed and some of the unchanged methyl hydrogen sulphate, this reaction also being reversible:



As a result of the balance of these reactions, it is found that the yield of methyl chlorosulphonate is only about half of the theoretical yield. *Methyl chlorosulphonate* is a colourless liquid and a violent lachrymator. It has b. p. 42°/16 mm., 134—135°/760 mm., D^{20}_4 1·514, D^{15}_4 1·492, n^{20}_D 1·414.

W. G.

Action of Chlorosulphonic Acid on Methyl Sulphate.
Preparation of Methyl Chlorosulphonate. R. LEVAILLANT and L.-J. SIMON (*Compt. rend.*, 1919, **169**, 234—236. Compare preceding abstract).—When heated together, methyl sulphate and chlorosulphonic acid react according to the equation



which is, however, reversible. Further, the methyl hydrogen sulphate formed, in its turn, reacts with the chlorosulphonic acid, as already seen. The yield from methyl sulphate is 70% of theory, and may be increased if the product is fractionally distilled, giving two fractions, *A*, containing methyl chlorosulphonate and a little chlorosulphonic acid, and *B*, containing chlorosulphonic acid, methyl chlorosulphonate, and methyl sulphate, this second fraction *B* being added to further quantities of the original reacting mixture.

W. G.

Preparation of the Fluorides of Organic Acids by means of Fluorosulphonic Acid and Fluorosulphonates. WILHELM TRAUBE and ANNA KRAHMER (*Ber.*, 1919, **52**, [*B*], 1293—1298).—The preparation of aliphatic acid chlorides by the action of heat on mixtures of salts of chlorosulphonic acid and fatty acids has been described by the Badische Anilin- & Soda-Fabrik (D.R.-P. 146690); the authors have attempted to prepare the fluorides by a similar method, but the results are not completely satisfactory. The best yields, obtained with fatty aromatic acids, do not exceed 20% of that theoretically possible, whilst with the simple aliphatic acids the yields fall as low as 5%. The by-products include considerable amounts of acid anhydrides. Better results are obtained by heating mixtures of fluorosulphonic acid and the fatty acid in a platinum vessel. The following substances are described: *β*-phenyl-propionyl fluoride, b. p. 96°/17 mm., which is only slowly decomposed by water; phenylacetyl fluoride, b. p. 88—89°/17 mm.; benzoyl fluoride, b. p. 156°; acetyl fluoride, b. p. 20·5°; propionyl fluoride, b. p. 44°; chloroacetyl fluoride, b. p. 74°; dichloroacetyl fluoride, b. p. 71—72°.

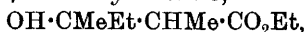
H. W.

Certain Aliphatic Compounds with Numerous Side-chains. RICHARD WILLSTÄTTER and DANIEL HATT (*Annalen*, 1919, **418**, 148—160).—The authors have synthesised *αβγδ*-tetramethylhexoic acid by way of the ester of the corresponding *β*-hydroxy-acid, the method employed consisting in union of a ketone and the ester of an *α*-halogenated aliphatic acid in presence of zinc (compare Reformatsky, *A.*, 1887, 717; 1896, i, 128) or magnesium (compare Zelinsky and Gutt, *A.*, 1902, i, 585). The synthesis in this way of ethyl *β*-hydroxy-*αβ*-dimethylvalerate from methyl ethyl ketone and ethyl *α*-iodopropionate occurs readily, but ethyl *isobutyl* ketone and ethyl *α*-iodopropionate yield, in addition to the ester of the *β*-hydroxy-acid, also that of the corresponding unsaturated acid. Hydrogenation of the latter in presence of platinum gives the *αβγδ*-tetramethylhexoic acid, which in habit resembles phytol derivatives, without, however, being identical with

any of these. The β -hydroxy-acid is converted by the action of 62%, or even more dilute, sulphuric acid into the highly stable γ -lactone, this behaviour being that exhibited by other alkylated $\alpha\beta$ -unsaturated acids.

$\beta\gamma$ -Dimethyl- δ -pentanone, obtained by boiling ethyl methylisopropylacetoacetate (compare van Romburgh, A., 1887, 232) with hydrobromic and glacial acetic acids, has b. p. 128—133·5°/719 mm. (van Romburgh gave 135—140°); its *oxime*, $C_{17}H_{15}ON$, is a colourless, viscous oil, b. p. 82—82·5°/10 mm., with an odour of peppermint. By sodium and alcohol, the ketone is reduced to $\beta\gamma$ -dimethyl- δ -pentanol, $C_7H_{16}O$, which is a somewhat viscous liquid, b. p. 149—150·5°/719 mm., D_4^{20} 0·836. δ -Iodo- $\beta\gamma$ -dimethyl-pentane, $C_7H_{15}I$, has b. p. 56—61°/11 mm., and smells like camphor.

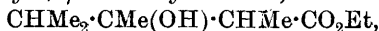
Ethyl β -hydroxy- $\alpha\beta$ -dimethylvalerate,



prepared from methyl ethyl ketone and ethyl α -iodopropionate in presence of magnesium, is a liquid, b. p. 78—79·5°/10 mm.

Ethyl $\alpha\beta$ -dimethyl- Δ^2 -butenoate, $CMeEt \cdot CMe \cdot CO_2Et$, prepared by heating the preceding ester with oxalic acid, is a mobile liquid, b. p. 64—66°/13·5 mm., D_4^{20} 0·927, with a pleasant odour and a vigorous reducing action on permanganate.

Ethyl β -hydroxy- $\alpha\beta\gamma$ -trimethylvalerate,



prepared from methyl isopropyl ketone and ethyl α -iodopropionate, is a mobile liquid, b. p. 90—93·5°/11·5 mm., $D_4^{17.5}$ 0·977; it is not converted into the corresponding unsaturated ester by either oxalic acid, phosphoric oxide, or phthalic anhydride. The free *hydroxy-acid*, $C_8H_{16}O_3$, forms a viscous liquid, b. p. 136—140°/9·5 mm., and in a desiccator, or more rapidly on heating with dilute sulphuric acid (1:1), is converted into $\alpha\beta\gamma$ -trimethyl- δ -valerolactone, $CHMe \cdot \begin{smallmatrix} CMe_2-O \\ | \\ CHMe \cdot CO \end{smallmatrix}$, which crystallises in needles and

lanceolate leaflets, m. p. 47·5°, b. p. 90·5—93°/10 mm., and has an intense menthol odour. When heated with hydriodic acid and phosphorus, the lactone gives an *aliphyl iodide* (? octyl iodide), b. p. 164—167·5°, and a very stable *carboxylic acid* of high molecular weight, b. p. 272—279°/10 mm. When heated for a day at 160—210° with hydriodic acid (D 1·96), the lactone loses carbon dioxide and yields a saturated *hydrocarbon*, b. p. 84—89°, which smells like petroleum and appears to have the composition of a cycloparaffin.

$\alpha\beta\gamma\delta$ -Tetramethyl- γ -hexolactone, $CHMe \cdot \begin{smallmatrix} CMePr^{\beta} \cdot O \\ | \\ CHMe \cdot CO \end{smallmatrix}$, is a somewhat viscous oil, b. p. 117—120°/12 mm., D_4^{20} 0·988, with an odour like that of menthol, and is only slowly oxidised by permanganate.

Tetramethyl- Δ^2 -hexenoic acid, $CHMe_2 \cdot CHMe \cdot CMe \cdot CMe \cdot CO_2H$, cannot be distilled even in a vacuum, owing to its ready conversion into the lactone, which forms slowly even at the ordinary tempera-

ture; the acid instantaneously combines with bromine and decolorises permanganate.

$\alpha\beta\gamma\delta$ -Tetramethylhexoic acid, $\text{CH}_3\cdot[\text{CHMe}]_4\cdot\text{CO}_2\text{H}$, is a somewhat viscous, colourless oil, b. p. $136-136.5^\circ/11$ mm., D_{20}^{25} 0.935, and smells faintly like turpentine. Its silver salt was analysed.

T. H. P.

Transformation of Acid Salts of Dibasic Acids in Aqueous Solution. TH. SABALITSCHKA (*Ber.*, 1919, **52**, [B], 1378—1384).—Previous experiments by Thoms and Sabalitschka (*A.*, 1917, i, 700) have shown that only minute traces of oxalic acid can be removed from aqueous solutions of potassium hydrogen oxalate by treatment with ether, this behaviour being in striking contrast with that observed with the acid salts of other dibasic organic acids. The author has therefore investigated the dialysis of solutions of potassium hydrogen oxalate of differing concentration and at differing temperatures. It is found that the diffusate invariably contains slightly more potassium in relationship to oxalic acid than is required for the acid salt, whilst the diffusing solution contains an excess of oxalic acid. It appeared probable that this is due to the existence of normal potassium oxalate and potassium tetroxalate in solutions of the hydrogen oxalate, and direct experimental evidence on this point is afforded by the crystallisation of potassium tetroxalate in the pure state from a not too concentrated solution of potassium hydrogen oxalate at $+10^\circ$. Solutions of ammonium hydrogen oxalate do not appear to behave in a similar manner.

It is pointed out that oxalic acid can be completely volatilised at the temperature of the boiling-water bath, and, further, that commercial potassium hydrogen oxalate does not generally correspond with the formula KHC_2O_4 .

H. W.

The Synthesis of Inositol Hexaphosphate and its Identity with the Phospho-organic Reserve Principle of Green Plants. S. POSTERNAK (*Compt. rend.*, 1919, **169**, 138—140. Compare this vol., i, 426).—Inositol hexaphosphate has been synthesised and isolated in the form of its double calcium sodium salt by heating inositol with phosphoric acid in the presence of phosphoric oxide at $120-130^\circ$ for three hours. The crystallographic properties of this synthetic double salt have been examined, and on comparison with those of the double salt prepared from phytin, the two sets of measurements were found to be identical. The crystals are monoclinic [$a : b : c = 0.630066 : 1 : 0.639015$ and $\beta = 108^\circ 13'$]. This is taken as conclusive proof that the phospho-organic reserve principle of green plants is inositol hexaphosphate.

W. G.

Improvements Relating to the Preparation of Amines. WILLIAM RINTOUL, JOHN THOMAS, and NOBEL'S EXPLOSIVES CO., LTD. (*Brit. Pat.*, 128372).—Secondary and tertiary amines

are separated from mixtures of the two containing an excess of the latter by treatment with carbonyl chloride at temperatures below 25° , whereby the secondary amine is converted into a carbamide chloride with the elimination of hydrogen chloride, which reacts, forming the hydrochloride of the tertiary amine. The reaction mixture is then treated with sufficient dilute hydrochloric acid to dissolve the whole of the tertiary amine, whilst the insoluble carbamide chloride is collected and boiled with either water or dilute hydrochloric acid to regenerate the secondary amine. In cases where the mixture of amines contains an excess of the secondary amine, the requisite excess of tertiary base is secured either by removing the secondary base in stages by repeating the above operation, or by actually adding a sufficient quantity of tertiary amine to the original mixture. [See, further, *J. Soc. Chem. Ind.*, 1919, September.] G. F. M.

Preparation of Aminosulphonic Acids by the Aid of Salts of Fluorosulphonic Acid. WILHELM TRAUBE and ELISABETH BREHMER (*Ber.*, 1919, 52, [B], 1284—1293).—The salts of fluorosulphonic acid possess the remarkable property of exchanging the fluorine atom for an amino-group when treated with an aqueous solution of the requisite base; under these conditions, a portion of the fluorosulphonic acid, greater or less according to the strength of the base, is hydrolysed to hydrofluoric and sulphuric acids, which represent the sole by-products of the change and which can readily be removed by chalk or barium hydroxide. The process has the considerable advantage over the older methods that it does not require the isolation of the base in the anhydrous condition. The following substances have been prepared in this manner: aminosulphonic acid, aminoethylaminosulphonic acid, barium hydrazinosulphonate, *potassium hydrazinosulphonate*, and *potassium methylaminosulphonate*, shining leaflets. *Methylaminosulphonic acid* forms long needles, m. p. 181° , and yields hygroscopic *ammonium* and *sodium* salts; the *barium* salt ($+H_2O$) is stable in air; the *silver*, *copper*, and *lead* salts are freely soluble in water. The action of potassium nitrite on an aqueous solution of methylaminosulphonic acid leads to the formation of *potassium methylnitrosoaminosulphonate*, $NO \cdot NMe \cdot SO_3K$, which, when reduced with zinc dust and acetic acid, and subsequently boiled with hydrochloric acid, gives methylhydrazine in 18% yield. Potassium ethylaminosulphonate is formed from potassium fluorosulphonate and ethylamine; the corresponding free acid forms clusters of needles, m. p. 167 — 168° . *Propylaminosulphonic acid*, *isobutylaminosulphonic acid*, and *isoamylaminosulphonic acid* are similarly prepared, and have m. p.'s 172 — 173° , 192° (decomp.), and 188° respectively; the *potassium* salts are described. Phenylaminosulphonic acid is obtained in 38% yield. *Sodium methylhydrazinosulphonate* closely resembles the corresponding ethyl compound; it could not, however, be transformed into the diazomethanesulphonate by oxidation with mercuric oxide. H. W.

α -Amino-alcohols with Secondary Alcohol Function.

ERNEST FOURNEAU and (MME.) PAULINE RAMART-LUCAS (*Bull. Soc. chim.*, 1919, [iv], **25**, 364—370).—Chloropropaldehyde readily reacts with magnesium alkyl bromides or iodides to give the corresponding secondary α -chloro-alcohols. These secondary alcohols condense with amines, such as dimethylamine, to give the α -amino-alcohols. The following compounds have been prepared.

α -Chloropentan- γ -ol, $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CHEt}\cdot\text{OH}$, b. p. $83\text{--}85^\circ/20\text{ mm.}$, $100^\circ/60\text{ mm.}$, $173^\circ/760\text{ mm.}$, giving an *acetyl* derivative, b. p. $89^\circ/15\text{ mm.}$, and a *benzoyl* derivative, b. p. $168^\circ/15\text{ mm.}$ α -Iodopentan- γ -ol, b. p. $105\text{--}108^\circ/15\text{ mm.}$, is obtained from the chloro-alcohol by the action of sodium iodide. With dimethylamine, α -chloropentan- γ -ol yields α -dimethylaminopentan- γ -ol, b. p. $175^\circ/760\text{ mm.}$, $97^\circ/46\text{ mm.}$ It gives a *hydrochloride* of its *benzoyl ether*, m. p. $120\text{--}121^\circ$, and a *hydrochloride* of its *p-nitrobenzoyl ether*, m. p. $145\text{--}146^\circ$. α -Diethylaminopentan- γ -ol has b. p. $76^\circ/13\text{ mm.}$, and yields the *hydrochloride* of its *benzoyl ether*, m. p. $106\text{--}107^\circ$, and the *hydrochloride* of its *methylcinnamyl ether*, m. p. 136° .

α -Chlorobutan- γ -ol, $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OH}$, b. p. $70^\circ/13\text{ mm.}$, gives α -dimethylaminobutan- γ -ol, b. p. $150^\circ/760\text{ mm.}$, yielding the *hydrochloride* of its *benzoyl ether*, b. p. $133\text{--}134^\circ$. α -Diethylaminobutan- γ -ol has b. p. $72^\circ/13\text{ mm.}$

α -Chlorohexan- γ -ol, $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CHPr}\cdot\text{OH}$, b. p. $90\text{--}91^\circ/13\text{ mm.}$, $120^\circ/35\text{ mm.}$, yields α -dimethylaminohexan- γ -ol, b. p. $193\text{--}194^\circ/760\text{ mm.}$, giving the *hydrochloride* of its *cinnamyl ether*, m. p. $134\text{--}135^\circ$.

α -Chloro- ζ -methylheptan- γ -ol, b. p. $110\text{--}115^\circ/13\text{ mm.}$, $128\text{--}130^\circ/25\text{ mm.}$, gives α -dimethylamino- ζ -methylheptan- γ -ol, b. p. $120^\circ/28\text{ mm.}$, yielding the *hydrochloride* of its *benzoyl ether*, m. p. $133\text{--}134^\circ$.

These chloro-alcohols, unlike those obtained from chloroacetone, are obtained quite pure and are very stable to light. W. G.

Carbamylglycollic Acids. ALFRED AHLQVIST (*J. pr. Chem.*, 1919, [ii], **99**, 45—84).—With carbamic acid, hydroxy-acids yield carbamates, for instance, $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CO}\cdot\text{NH}_2$, which are at the same time acids and urethanes, and are most suitably named carbamic ester acids, the term urethane acids being better applied to acids of the type $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}_2\text{R}$. Few of these carbamic ester acids being known (compare Thiele and Dent, A., 1899, i, 14; Lambling, A., 1898, i, 588; 1899, i, 52, 84; 1902, i, 537, 603, 756), the author has made a more extended investigation of them. Oxidation of the corresponding thiocarbamyl compounds by means of bromine or permanganate affords a convenient general method for the synthesis of these acids (compare Holmberg, A., 1905, i, 324; 1907, i, 384; 1910, i, 834; 1912, i, 131), and the author has studied the methods of preparing the thiocarbamylglycollic acids necessary for this synthesis.

Acetaminocarbothiolonglycollic [monoamide of xanthodiacetic]

acid, $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CS}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$, prepared as sodium salt according to the scheme $\text{CO}_2\text{Na}\cdot\text{CH}_2\cdot\text{OH} + \text{CS}_2 + \text{KOH} = \text{H}_2\text{O} + \text{CO}_2\text{Na}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CS}\cdot\text{SK}$, and this

$+ \text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NH}_2 \rightarrow \text{CO}_2\text{Na}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CS}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$, crystallises in faint yellow prisms and sinters at 123° , m. p. (not sharp) $129\text{--}130^\circ$.

Trithiocarbodiglycollamide, $\text{CS}(\text{S}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2)_2$, formed during the above synthesis by the action of chloroacetamide on trithiocarbonate derived from the carbon disulphide and alkali, crystallises in golden spangles, m. p. $206\text{--}207^\circ$ (decomp.) or 198° (slow heating).

Thiocarbamyglycollic acid is formed in best yield from ethylcarbothiolonglycollic acid (compare Holmberg, A., 1907, i, 384), but is more readily obtained pure, as ammonium salt, by the action of ammonia (3 mols.) on the monoamide of xanthodiacetic acid (1 mol.). The ammonium salt forms white needles, m. p. about 160° (decomp.). The free acid shows m. p. 125° , or, with rapid heating, $134\text{--}135^\circ$, the varying values being caused by conversion of the acid to a greater or less extent into the anhydride; the temperature, $111\text{--}112^\circ$, given by Holmberg as the melting point of the acid is really that of the anhydride (see below). The ammonium salt formed in the above way is accompanied by dithioglycollamide, $\text{S}_2(\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2)_2$, m. p. $157\cdot5\text{--}158\cdot5^\circ$ (Clæsson, A., 1881, 580, gave m. p. 155°), which results from the oxidation in the air of thioglycollamide (compare Klason and Carlson, A., 1906, i, 232), this being also a product of the decomposition of the monoamide of xanthodiacetic acid by ammonia.

The action of ammonia on carbothiolondiglycollic acid yields, besides the ammonium salt of thiocarbamyglycollic acid, also that of trithiocarbodiglycollic acid, $\text{CS}(\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$, m. p. $172\text{--}173^\circ$ (compare Holmberg, A., 1905, i, 324).

Thiocarbamyglycollic anhydride [4 - keto - 2 - thionoxazolidine], $\text{O} < \begin{array}{c} \text{CH}_2\cdot\text{CO} \\ \text{CS}\text{--}\text{NH} \end{array}$, forms a woolly mass of soft, hair-like crystals, m. p. $111\text{--}112^\circ$, and is not converted into the corresponding acid on dissolution in water. The compound, m. p. 143° , obtained by heating thiocarbamyglycollic acid with acetic anhydride, and described by Holmberg (A., 1909, i, 286; 1912, i, 130) as this anhydride, consists of carbamyglycollic acid. In virtue of its iminic hydrogen, the anhydride exhibits acid characters, and may be determined titrimetrically.

Ethylthiocarbamyglycollic anhydride [4-keto-2-thion-3-ethyl-oxazolidine] (compare Holmberg, A., 1912, i, 131), prepared by the action of ethylamine on either carbothiolondiglycollic acid or the monoamide of xanthodiacetic acid, forms crystals, m. p. $40\text{--}40\cdot5^\circ$, and is accompanied by thioglycollic acid, b. p. $107\text{--}108^\circ/16\text{ mm.}$ When converted by alkali into a salt of the corresponding acid and oxidised by means of bromine, it yields ethylcarbamyglycollic acid, m. p. $87\text{--}88^\circ$.

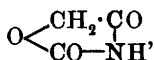
Diethylthiocarbamyglycollic acid, crystals, m. p. $90\cdot5\text{--}91^\circ$, is

obtained by the action of diethylamine on either ethylcarbothiolonglycollic acid or carbothiolonglycollic acid or its mono-amide; the product obtained from the last two acids crystallises well and is accompanied by thioglycollic acid.

In preparing carbamylglycollic acids from the corresponding thiocarbamylglycollic acids, the best oxidising agent is bromine, the action of permanganate resulting in poor yields and often in impure products.

Carbamylglycollic acid thus obtained melts at temperatures varying from 155° to 161° , according to the rapidity of heating, the acid undergoing more profound change than mere conversion into anhydride. The potassium, barium ($+H_2O$), and silver salts, and the ethyl ester, m. p. $64-65^{\circ}$ (Thiele and Dent, *loc. cit.*, give 61°), were prepared. When heated in aqueous solution, the acid decomposes into glycollic acid, carbon dioxide, and ammonia.

Carbamylglycollic anhydride (2:4-diketo-oxazolidine),



m. p. $89-90^{\circ}$, cannot be obtained by heating the corresponding acid, but may be prepared by oxidation of thiocarbamylglycollic anhydride by means of bromine (compare Traube and Ascher, A., 1913, i, 901). It exhibits acid properties, and when titrated with barium hydroxide solution gives a sharp colour change with phenolphthalein. When heated in aqueous solution or in presence of acid, the anhydride undergoes no appreciable decomposition, and the ammonia evolved on distillation with concentrated alkali hydroxide is less than the calculated quantity.

Ethylcarbamylglycollic acid, prepared from ethylthiocarbamylglycollic anhydride by the action of bromine or permanganate in potassium hydroxide solution, has m. p. $87-88^{\circ}$ (Holmberg, A., 1912, i, 131, gave $85-86^{\circ}$). The potassium, barium ($+H_2O$), and silver salts, the *ethyl* ester, $\text{CO}_2\text{Et} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{CO} \cdot \text{NH}\text{Et}$, m. p. $46-47^{\circ}$, and the *amide*, $\text{C}_5\text{H}_{10}\text{O}_3\text{N}_2$, m. p. $120.5-121.5^{\circ}$, were prepared. When heated in aqueous solution or in presence of acid, the acid decomposes, with formation of glycollic acid, carbon dioxide, and ethylamine; with concentrated alkali hydroxide, the decomposition is quantitative.

Ethylcarbamylglycollic anhydride [2:4-diketo-3-ethylloxazolidine], $\text{O} < \begin{array}{c} \text{CH}_2 \cdot \text{CO} \\ | \\ \text{CO} - \text{NEt}' \end{array}$ forms a colourless oil with a characteristic odour,

b. p. $119.5^{\circ}/12$ mm., D_4^{20} 1.246, n_D^{18} 1.462. By cold barium hydroxide solution, it is decomposed, apparently, into glycollethylamide, $\text{NH}\text{Et} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{OH}$, but when heated in aqueous or acid solution it remains almost entirely undecomposed. The methylene group of the anhydride does not react with benzaldehyde in presence of acetic anhydride in the same way as that of ethyl- and phenyl-thiocarbamylglycollic anhydrides (compare Holmberg, A., 1912, i, 133), the only separable product of the reaction being benzyldene acetate.

Diethylcarbamylglycollic acid, $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{CO} \cdot \text{NEt}_2$, prepared

by the action of either bromine in alkaline solution or permanganate on diethylthiocarbamyglycollic acid, forms colourless needles, m. p. 77·5—79°; the *potassium*, *barium*, and *silver* salts are described. The *ethyl* ester, $C_9H_{17}O_4N$, is a mobile liquid with a characteristic, fruity odour, b. p. 122—123°/10 mm., D_4^{20} 1·059 n_D^{17} 1·433. Attempts to prepare the amide of the acid resulted in the formation of an uncrystallisable, viscous product, which was not analysed. When heated in aqueous solution or in neutral, acid, or alkaline solution, the acid decomposes into glycollic acid, carbon dioxide, and amine. T. H. P.

Electrolytic Reaction of Organic Sulphur Compounds.

I. Thioamide Group. MOTOOKI MATSUI and EITARO ASHIDA (*J. Tokyo Chem. Soc.*, 1919, **40**, 147—156).—A compound like carbamide, containing the carbamyl group, is known to react as an imino-compound. According to Werner, the iminocarbamic acid formula expresses the true nature of carbamide. Matsui previously showed (*ibid.*, **30**, 1157) that thioamide groups must be represented by the imino-formula, $RC(:NH) \cdot SH$. As a further proof for this contention, he and Ashida argue that if the thioamide group acts as an imino-acid, then electrolytic oxidation ought to produce a double sulphur compound, containing two groups of $>C(:NH)$ and $-SC(:NH)-$. Experimental results seem to confirm their hypothesis. To 1·32 grams of thiocarbamide in 106 c.c. of alcohol are added 4 c.c. of nitric acid (D 1·22). After passing a current of 0·3 to 0·4 ampere for five hours, there appears at the positive platinum pole a white, needle-shaped compound, yielding 1·06 grams after repeated purifications. Analysis shows it to be dithioformamidine dinitrate, $[SC(:NH) \cdot NH_2]_2 \cdot 2HNO_3$. From acetylthiocarbamide they obtained dithiomonoacetylformamidine. From monophenylthiocarbamide, $H_2N \cdot C(:NPh) \cdot S \cdot C(:NH) \cdot NH_2$, is obtained. Thiobenzamide in alcohol is known to be oxidised by iodine to 3:5-diphenyl-1:2:4-thiodiazole. By electrolytic oxidation, they obtained the identical compound, namely, $S < \begin{smallmatrix} N \\ \parallel \\ CPh \end{smallmatrix} \begin{smallmatrix} \parallel \\ N \end{smallmatrix} Ph$, m. p. 90°, instead of the dithio-compound. In the same way, thioacetanilide yields $C_6H_4 < \begin{smallmatrix} S \\ \parallel \\ N \end{smallmatrix} \begin{smallmatrix} \parallel \\ N \end{smallmatrix} CMe$. Although, thus, they failed to obtain dithio-compounds in the last two cases, still they believe that the reactions in every case could be explained only on the assumption that the thioamide group has the structure $RC(:NH) \cdot SH$.

CHEMICAL ABSTRACTS.

The Catalytic Reduction of Hydrogen Cyanide. SYDNEY BARRATT and ALAN FRANCIS TITLEY (T., 1919, **115**, 902—907).

New Method of Preparation of some Polynitro-aromatic Compounds. MARQUEYROL and LORLETTE (*Bull. Soc. chim.*, 1919, [iv], **25**, 370—375).—For the preparation of compounds of the type

of trinitrophenol, the authors recommend that the nitration should be carried out in three stages. The phenol ($\frac{1}{2}$ mol.) is converted into *p*-phenolsulphonic acid, which is then diluted with water and poured into a cold aqueous solution of sodium nitrate, the product being sodium 2-nitrophenol-4-sulphonate. To this solution, nitric acid ($\frac{1}{2}$ mol.) is then added, a mixture of 2:4-dinitrophenol and sodium 2:6-dinitrophenol-4-sulphonate being obtained. After cooling, the dinitrophenol is separated by filtration, and may be further nitrated, and to the filtrate more nitric acid ($\frac{1}{2}$ or 1 mol.) is added, and the liquid brought to the boil. By this means, very pure picric acid is obtained with a good yield. This procedure is of advantage in that practically no nitrous fumes are liberated, and but little more than the theoretical quantities of sulphuric and nitric acids are required.

This method may be applied to commercial cresol. In the first stage, any *o*-cresol present yields *o*-cresol-5-sulphonic acid, the *m*-cresol gives *m*-cresol-6-sulphonic acid, and the *p*-cresol gives *p*-cresol-3-sulphonic acid. In the next stage, from these sulphonic acids are formed, respectively, the 3-nitro-derivative, a mixture of the 2-nitro- and 4-nitro-compounds, and the 5-nitro-derivative. In the third stage, the *o*- and *p*-cresols will yield simply their 3:5-dinitro-derivatives, which are insoluble in water, and may be filtered off, whilst from the *m*-cresol there is obtained sodium 2:4-dinitro-*m*-cresol-6-sulphonate, which is soluble. The latter compound, when boiled with nitric acid, gives trinitro-*m*-cresol.

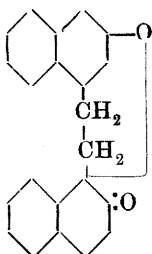
It is suggested that the nitrosulphonic acids of the three cresols may be separated through their potassium salts, since that from *p*-cresol is only sparingly soluble in water and is formed in the cold; that from *o*-cresol is only sparingly soluble, and is not formed in the cold, but only at 50°; whilst that from *m*-cresol is soluble in water and is only formed at 60°.

W. G.

Preparation of 2:4-Dinitrophenol by Direct Nitration of Phenol. MARQUEYROL and LORLETTE (*Bull. Soc. chim.*, 1919, [iv], 25, 375).—If phenol is liquefied by the addition of 30 grams of water to 94 grams of the phenol, and this liquid is slowly added to a mixture of 400 c.c. of sulphuric acid (D 1.58) and 270 c.c. of nitric acid (D 1.33), kept well stirred, and cooled until the whole of the phenol is added, the temperature then being allowed to rise to 100°, a yield of 71% of 2:4-dinitrophenol is obtained. W. G.

Oxidation of Phenols. III. Polymerisation of Methylenequinones to Cyclic Dehydrophenols. RUDOLF PUMMERER and EMIL CHERBULIEZ (*Ber.*, 1919, 52, [B], 1392—1402).—Dehydro-1-methyl- β -naphthol is decomposed when heated in xylene solution into 1-methyl- β -naphthol and naphthamethylenequinone, which could not be obtained in the unimolecular state (A., 1915, i, 419); this substance has now been obtained in the form of sulphur-yellow crystals, m. p. 143° (corr.), and is shown to be formed by the condensation of two molecules of the methylenequinone. It appears

to be dehydro- $\alpha\beta$ -dinaphthol-2-ethane (annexed formula), since it yields a *monophenylhydrazone*, shining platelets, m. p. 233° (corr.), and is reduced by zinc dust and acetic acid to $\alpha\beta$ -dinaphthol-2-ethane, m. p. 253° (corr.) (*diacetyl* derivative, monoclinic plates, m. p. 233 — 234° [corr.]), which is readily reconverted into dehydrodinaphthoethane by oxidation with potassium ferricyanide in dilute alkaline solution.



Dehydro-6-bromo-1-methyl- β -naphthol (*loc. cit.*) is similarly decomposed by boiling xylene, yielding bromomethylnaphthol and *dehydrodibromodinaphthoethane*, yellow prisms, m. p. 177° (corr.).

The latter gives a *monophenylhydrazone*, small, reddish-brown needles, m. p. 237 — 238° (corr.), and is reduced to 6:6'-dibromo- $\alpha\beta$ -dinaphthol-2-ethane, needles, m. p. 275° (corr.), which is readily re-oxidised to the parent substance.

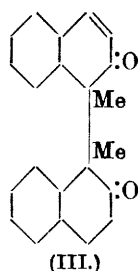
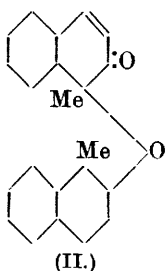
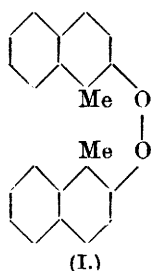
Zincke's tetrachloro-*p*-methylenbenzoquinone (A., 1903, i, 757) has been shown to be dehydro-tetrachloro-*p*-cresol (*loc. cit.*) from a study of its power to oxidise quinol; this conclusion is now confirmed by observations of its oxidising action on potassium iodide. Determinations of molecular weight in benzene show an almost complete dissociation of the double molecule either into the radicles, or, more probably, into the methylenequinone and tetrachloro-*p*-cresol.

The authors' investigations lead them to consider that the true methylenequinones with an unsubstituted methylene group are exceedingly active substances which readily polymerise. They are therefore of the opinion that the seven compounds described as such in the literature are either quinol ethers or dehydro-substances, and that a methylenequinone with unsubstituted methylene group has not up to the present been isolated in the unimolecular condition.

H. W.

Oxidation of Phenols. IV. Constitution of the Dehydronaphthols and Preparation of Dehydro- α -bromo- β -naphthol.

RUDOLF PUMMERER (*Ber.*, 1919, 52, [B], 1403—1413).—The three following formulæ are possible for dehydro-1-methyl- β -naphthol (compare A., 1915, i, 418):

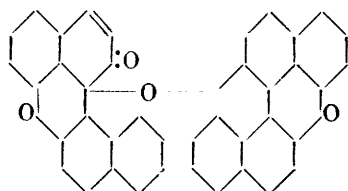


The first explains the ready union of the substance with tri-

phenylmethyl, but is improbable by reason of the yellow colour of the substance and its instability towards permanganate in acetone solution at -40° . The decision between II and III cannot be made with phenylhydrazine, which behaves as a reducing agent. The author has therefore prepared an α -halogen-substituted dehydro- β -naphthol in which, according to II, two halogen atoms must be loosely combined, whilst, according to III, only one is in loose combination. *Dehydro- α -bromo- β -naphthol*, m. p. $115-116^{\circ}$, is prepared by the action of tetrachlorodehydro-*p*-cresol on 1-bromo- β -naphthol; it contains only one reactive bromine atom, since it is hydrolysed in aqueous-alcoholic solution to β -naphthaquinone and 1-bromo- β -naphthol, and is reduced by stannous chloride probably to α' -bromo- β -hydroxy- $\alpha\beta'$ -dinaphthyl ether, m. p. $135.5-136.5^{\circ}$ (corr.), in which the α -position adjacent to the hydroxyl group must be occupied, since it does not yield an azo-dye with benzenediazonium chloride. The dibromo-compound must therefore have a constitution analogous to that expressed by formula II.

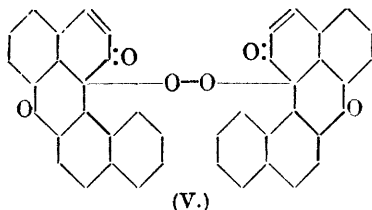
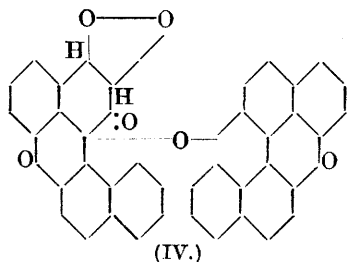
β -Hydroxy- $\alpha\beta'$ -dinaphthyl ether is obtained, amongst other products, by the dehydrogenation of β -naphthol by potassium ferricyanide in alkaline solution (compare following abstract); the first product is probably dehydro- β -naphthol, the keto-form of which is not stable and passes into the corresponding enolic form.

The constitution of dehydro-oxydinaphthalene oxide (Pummerer and Frankfurter, A., 1914, i, 714) is further discussed. It readily decolorises potassium permanganate, and hence cannot be an aromatic peroxide; the diketo-formula is also impossible, for reasons previously given, so that there remains only the annexed formula.



When treated with benzoyl peroxide (subsequent abstract), it absorbs two atoms of oxygen, yielding a compound which is termed a β -peroxide (IV), to distinguish it from the α -peroxide (V) obtained with oxygen. The β -derivative is sharply distinguished from the α -compound by its stability towards

permanganate in pyridine solution and by the lemon-yellow colour



common to all *O*-derivatives of hydroxydinaphthalene oxide, whereas the *C*-derivative (α -peroxide) is pale brown. The β -per-

oxide can only be obtained from the solid dehydro-substance; solutions of the latter, even when concentrated, are rapidly decolorised by benzoyl peroxide without separation of the β -peroxide, whilst the α -peroxide is contained among the products, its formation being primarily due to the dissociation of the dehydro-substance into its component radicles (Pummerer and Frankfurter, *loc. cit.*); the possible tautomerism of the latter is again discussed, and the hypothesis advanced previously (*loc. cit.*) satisfactorily explains the more recent phenomena. H. W.

Oxidation of Phenols. V. Formation of β -Hydroxy- $\alpha\beta'$ -dinaphthyl Ether by the Dehydrogenation of β -Naphthol. RUDOLF PUMMERER and EMIL CHERBULIEZ (*Ber.*, 1919, 52, [B], 1414—1415. Compare preceding abstract).—Oxidation of a solution of β -naphthol in the requisite quantity of aqueous sodium hydroxide solution by means of aqueous potassium ferricyanide leads to a mixture of products from which β -hydroxy- $\alpha\beta'$ -dinaphthyl ether, colourless needles, m. p. 196° , can be isolated in small amount. H. W.

Oxidation of Phenols. VI. Dehydro-oxydinaphthalene Oxide and Colorimetric Observations of its Dissociation into Radicles. RUDOLF PUMMERER and FRITZ FRANKFURTER (*Ber.*, 1919, 52, [B], 1416—1420. Compare preceding abstracts).—The β -peroxide of dehydro-oxydinaphthalene oxide is prepared by the action of a concentrated solution of benzoyl peroxide in benzene on dehydro-oxydinaphthalene oxide at the ordinary temperature; it forms lemon-yellow, microscopic prisms, m. p. 210° (corr.; decomp.), which are reduced by zinc dust and acetic acid to hydroxydinaphthalene oxide; the latter is also obtained by reduction of the α -peroxide.

The dilutions at which dehydro-oxydinaphthalene oxide is completely dissociated into its radicles have been colorimetrically estimated for a number of solvents (chloroform, benzene, xylene, ethyl ether, ethyl acetate, carbon disulphide, nitrobenzene); the dielectric constant of the solvent appears to have little influence on its dissociating power. H. W.

Compounds of Arsenic Acid and Catechol. R. F. WEINLAND and JOSEF HEINZLER (*Ber.*, 1919, 52, [B], 1316—1329).—*Catechol semiarsonate*, $\text{AsO}(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{OH})_3\cdot 4\text{H}_2\text{O}$, m. p. about 103° after softening at 60° , is readily obtained in large, colourless crystals when concentrated aqueous solutions of arsenic acid and catechol in molecular proportions varying from $1:\frac{1}{2}$ to $1:3$ are mixed. It is slowly hydrolysed in dilute aqueous solutions, more readily in the presence of acids, and is not decomposed by short heating with alkalis. It is stable in diffused light, but darkens on exposure to direct sunlight. It forms beautifully crystalline salts, in which it appears to function as a monobasic acid as far as the experimental evidence at present shows. When titrated with alkali in the

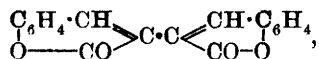
presence of phenolphthalein, the colour change occurs after addition of exactly one equivalent of base, with methyl-orange at a slightly earlier stage; the acid thus appears to be weaker than arsenic acid. The salts are generally prepared by the addition of the base or of a suitable salt of the metal to a concentrated aqueous solution of the acid. The following salts are described: *ammonium* salt, $\left[\text{AsO}(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{O})_3\right]_{\text{H}_2}^{\text{NH}_4}$, plates; *potassium* salt, plates or rods; *sodium* salt ($2\text{H}_2\text{O}$), rods, anhydrous, prisms; *silver* salt, minute crystals, very sparingly soluble in water and not sensitive to light; *magnesium* salt ($8\text{H}_2\text{O}$); *calcium* salt ($8\text{H}_2\text{O}$); *barium* salt ($8\text{H}_2\text{O}$); *zinc* salt ($8\text{H}_2\text{O}$); *ferrous* salt ($8\text{H}_2\text{O}$); *nickel* salt ($8\text{H}_2\text{O}$); *cobalt* salt ($8\text{H}_2\text{O}$). With the exception of the barium compound, the salts generally crystallise in cubes. The estimation of water of crystallisation is rendered a little uncertain by the difficulty of drying the substances without decomposition.

If a considerable excess of catechol is used in the preparation of the ammonium or potassium salts, compounds of the formula $3[\text{AsO}(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{O})_3]\text{K}(\text{NH}_4)\text{H}_2\text{C}_6\text{H}_4(\text{OH})_2$ are obtained; catechol is liberated when they are dissolved in hot water, and primary catechol arsenates are formed.

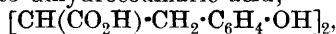
Another *ammonium* salt, which appears to have the composition $3[\text{AsO}(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{O})_3]\text{H}_3\cdot 7\text{NH}_3$, is also described, but the exact analysis is difficult, as it loses ammonia at the ordinary temperature.
H. W.

The Reduction of *allocinnamic* Acid and Coumarin.

YASUHIKO ASAHINA and ATSUSHI FUJITA (*J. Pharm. Soc. Japan*, 1919, No. 444, 97—109).—By reduction of methyl *allocinnamate* with sodium amalgam, phenylpropionic acid (43%), β -diphenyl-adipic acid, m. p. 175° (6%), and the corresponding *iso*-acid, m. p. 75° (3%), were obtained as their methyl esters. Henle (A., 1906, i, 669), using aluminium amalgam, obtained 55%, 8—9%, and 4—5%, respectively, of the same compounds by reduction of methyl cinnamate. This shows that *allocinnamic* and cinnamic acids yield essentially the same reduction products. Sodium amalgam is a better reducing agent than aluminium amalgam, since it reacts more rapidly, and the precipitation of aluminium hydroxide is avoided. Coumarin, as a derivative of *allocinnamic* acid, yields bimolecular reduction products. Dyson (T., 1887, 51, 68) obtained from salicylaldehyde and sodium succinate a dicoumarin,



which he reduced to dihydrocoumaric acid,



and to dihydrocoumarin, m. p. $222\text{—}224^\circ$. Fries and Fickewirth (A., 1908, i, 822) obtained, by reduction of coumarin and dehydration of the resulting tetrahydrodicoumaric acids, two tetrahydrodicoumarins, m. p. 284° and 256° respectively. The former they

designated α , the latter β , and to the acids they assigned the Dyson dihydrocoumaric acid formula shown above. This formulation is incorrect; two coumarin nuclei must necessarily unite in the β -position, whereas Dyson's dihydrocoumarin is linked in the α -position. Its reduction products are derivatives of succinic acid, whilst the products of direct reduction of coumarin are $\beta\gamma$ -disubstituted adipic acids. This was established experimentally by repeating Fries and Fickewirth's preparation of the tetrahydrocoumarins, which were obtained with m. p. 284° and 256° , just as described by those authors, and comparing them with reduction products of dicoumarin prepared as described by Dyson. The latter process yielded two dihydrocoumarins, m. p. 243° and 248° respectively, but when mixed they had m. p. 222 — 224° . It was evidently this mixture which Dyson obtained. Neither is identical with either of the tetrahydrocoumarins of Fries and Fickewirth. It is therefore proposed to call Dyson's compound α -dicoumarin, and the two derivatives (of which he had the mixture) α - and β -tetrahydro- α -dicoumarin. The tetrahydro-derivatives of Fries and Fickewirth are, then, to be considered as derivatives of an unknown β -dicoumarin.

CHEMICAL ABSTRACTS.

The Acylsemicarbazides and the Acylhydroxamides (Rectification). J. BOUGAULT (*Bull. Soc. chim.*, 1919, [iv], 25, 384—386).—As a result of further analyses, the author now finds that the compounds obtained by the action of iodine and sodium carbonate on the semicarbazones and oximes of α -ketonic acids, and previously described as acylsemicarbazides and acylhydroxamides (compare A., 1916, i, 764, 765; 1917, i, 417, 688, 694), do not possess the constitution then assigned to them. Instead of a molecular composition, $R\cdot CO\cdot NH\cdot NH\cdot CO\cdot NH_2$, as given to the acylsemicarbazides, the elements of a molecule of water should be deducted, giving an empirical formula $R\cdot C_2H_2ON_3$, the constitution of which has not been elucidated. Similarly, where the acylhydroxamides were assigned the constitution $R\cdot CO\cdot NH\cdot OH$, the formula should now be written $R\cdot CON$, and their constitution is considered to be either $\begin{array}{c} CPh\cdot CPh \\ || \quad || \\ NO\cdot ON \end{array}$ or $\begin{array}{c} CPh\cdot CPh \\ | \\ N\cdot O\cdot N \end{array} > O$. It has been shown that the so-called acylhydroxamide obtained from phenylglyoxylic acid is identical with diphenylglyoxime peroxide.

W. G.

Truxillic Acids and Truxones. R. STOERMER and G. FOERSTER (*Ber.*, 1919, 52, [B], 1255—1272).—The recent publication of Stobbe (this vol., i, 329) has induced the authors to describe a series of experiments which are still partly unfinished.

allo-Cinnamic acid is transformed by the light of a quartz lamp into β -isotruxillic acid; in sunlight, the same acid is also formed, occasionally accompanied by α -truxillic acid. Depolymerisation of β -isotruxillic and α -truxillic acids occurs when solutions of their sodium salts are exposed to the light of a quartz lamp, *trans*- and *allo*-cinnamic acids being formed from the former acid, cinnamic

and, possibly, *allocinnamic* and γ -truxillic acids from the latter acid. Attempts to polymerise crotonic, fumaric, β -phenylcinnamic, and *cis*- or *trans*-*p*-methoxycinnamic acids by sunlight were unsuccessful; β -methylcinnamic acid, however, gave dimethyltruxillic acid, m. p. 217—218°.

α -Truxone, m. p. 293°, is conveniently prepared by the action of aluminium chloride on a solution of α -truxillyl chloride in carbon disulphide; the dioxime, m. p. above 300°, is converted by methyl sulphate into the *dimethyl ether*, m. p. 214°. The molecular weight of the latter has been determined in benzene solution, and the results confirm the formula, $(C_9H_6O)_2$, for truxone. γ -Truxillic acid could not be converted into a truxone by sulphuric acid, but yielded α -truxone with aluminium chloride; β - and δ -isotruxillic acids were either unchanged or merely sulphonated by sulphuric acid.

α - and γ -*Diphenyltruxones* are prepared by the action of fuming sulphuric acid on β -phenylcinnamic acid or β -hydroxy- β -phenylhydrocinnamic acid, and are separated by fractional crystallisation from acetone or from a mixture of alcohol and acetic acid; the former crystallises in rods or plates, m. p. 253°, whilst the latter has m. p. 224°, and is converted when heated at about 225° into the α -derivative. The following derivatives are described: *α -diphenyltruxone monoxime*, six-sided crystals, m. p. 273·5° (*methyl ether*, colourless needles, m. p. 208°); *α -diphenyltruxone dioxime*, needles, m. p. 262°; *γ -diphenyltruxone monoxime*, needles, m. p. 235° (*methyl ether*, m. p. 170°); *γ -diphenyltruxone dioxime*, m. p. 270·5—271°. The hydroxylamino-group is readily removed by treatment of the oximes with alcohol at 100°, the corresponding truxones being regenerated. *α -Diphenyltruxone monophenylhydrazone* forms yellow crystals, m. p. 153—154°, whilst the monophenylhydrazone of the γ -compound has m. p. 128—129°. Attempts to reduce the truxones completely by Clemmensen's method, by sodium amalgam, zinc and acetic acid, or zinc and potassium hydroxide were unsuccessful, the process coming to an end with the production of the diol. In these circumstances, γ -diphenyltruxone yields *α -diphenyltruxandiol*; isomerisation is not induced by hydrochloric acid or potassium hydroxide alone, so that the nascent hydrogen appears to have an isomerising as well as a reducing action. *α -Diphenyltruxandiol* has m. p. 234·5°; the *monoacetate* (possibly not quite pure) melts at 235—237°, the *diacetate* at 215—216°. The α - and γ -*diphenyltruxanes* were, however, prepared from the corresponding truxones by the action of hydrazine and sodium ethoxide; the former has m. p. 201—202°. *γ -Diphenyltruxone dihydrazone* forms small crystals, m. p. 254°, and is converted by sodium ethoxide into a mixture of α -diphenyltruxane and γ -diphenyltruxane, m. p. about 169—171° but the latter could not be prepared in the pure condition on account of lack of material. The latter is completely converted into the α -isomeride when heated for five hours at a temperature slightly above its melting point.

H. W.

Constitution of Bile Acids. II. Dehydrocholanic Acid.

W. BORSCHÉ (*Ber.*, 1919, **52**, [B], 1353—1365. Compare Borsche and Rosenkranz, this vol., i, 276).—Further experiments with dehydrocholanic acid lead the author to adopt Schenk's view of its constitution, and thus to consider it as a triketocarboxylic acid containing the $\cdot\text{CO}\cdot\text{CH}_3$ group; all attempts to identify the presence of an aldehydic group were unsuccessful, whilst it has been found possible to condense the substance with aromatic aldehydes, thus obtaining conclusive evidence of the presence of the $\cdot\text{CO}\cdot\text{CH}_3$ group. One of the carbonyl groups of dehydrocholanic acid is more reactive than the remaining two, and thus gives rise to acetals when the acid is esterified, whilst also it is the first to suffer reduction; the compound thus formed, which was previously described as deoxy-dehydrocholanic acid, is now designated β -dehydrodeoxycholanic acid, to avoid confusion with the primary product of the oxidation of deoxycholanic acid.

Methyl dehydrocholanate, $\text{C}_{25}\text{H}_{36}\text{O}_5$, is prepared by the esterification of dehydrocholanic acid in the presence of a considerable amount of hydrogen chloride or sulphuric acid; it crystallises in silky needles, m. p. 241—242°, which are very sparingly soluble in methyl alcohol. It forms a *trioxime*, leaflets, m. p. 265—266°, and a *triacetyl* derivative, which gradually melts from about 60°. *Methyl dehydrocholanate dimethylacetal*, $\text{C}_{27}\text{H}_{42}\text{O}_6$, is formed by treating the ester or the acid with methyl alcohol containing 1% of hydrogen chloride or 3% of sulphuric acid; it forms long needles, m. p. 140°, and is freely soluble in warm methyl alcohol. It is reconverted into the ester by concentrated methyl-alcoholic solutions of mineral acids, and is hydrolysed to dehydrocholanic acid by alkali. With hydroxylamine, it gives the trioxime of methyl dehydrocholanate. The acetal nature of the substance is proved by the fact that methyl alcohol is readily eliminated when it is heated, and that it yields an *enol ether*, $\text{C}_{26}\text{H}_{33}\text{O}_5$, colourless leaflets, m. p. 173—174°, b. p. 333—334°/16 mm. Methyl-alcoholic potassium hydroxide solution converts it into dehydrocholanic acid, whilst hydroxylamine transforms it into the trioxime of methyl dehydrocholanate. It readily absorbs bromine, but methyl bromide appears to be eliminated simultaneously. A similar substance, m. p. 170—172° (decomp.), appears to be formed by the action of a 2% solution of sulphuric acid in ethyl alcohol on dehydrocholanic acid, but the product is readily converted into ethyl dehydrocholanate, m. p. 221°.

β -Deoxydehydrocholanic acid, needles, m. p. 176°, is prepared mixed with unchanged acid, and cholanecarboxylic acid by the reduction of dehydrocholanic acid by amalgamated zinc and hydrochloric acid; it crystallises also with $1\text{H}_2\text{O}$, m. p. 115°. The *ethyl* ester crystallises in colourless needles, m. p. 152—153°, and yields a *dioxime*, pearly leaflets, m. p. 242° (decomp.).

Cholanecarboxylic acid, m. p. 160°, is obtained in 55—60% yield by the reduction of dehydrocholanic acid by Clemmensen's method. The following derivatives have been prepared: *ethyl* ester, colour-

less, coarse needles, m. p. 92° ; *chloride*, m. p. 128° ; *amide*, minute, hexagonal prisms, m. p. 75° . H. W.

Preparation and Uses of Semi-oxamazide. L. G. RADCLIFFE (*Perfumery and Essen. Oil Rec.*, 1919, **10**, 39—42).—During a study on certain aromatic aldehydes, it became necessary to prepare their semi-oxamazones, and preliminary thereto the requisite semi-oxamazide. Detailed descriptions are accordingly given for the preparation of ethyl oxalate, oxamethane, and the finished reagent. Many of the semi-oxamazones described had been previously prepared by Kerp and Unger (A., 1897, i, 269), and include those of benzaldehyde, *p*-toluic, *p*-isopropylbenzoic, anisic, cinnamic, salicylic and phenylacetic aldehydes, vanillin, piperonal, citral and furfuraldehyde, acetophenone, phenyl ethyl ketone, styryl methyl ketone, benzophenone, and menthone. CHEMICAL ABSTRACTS.

A New Method of Obtaining Bicyclic Ketones. FÉLIX TABOURY and MARCEL GODCHOT (*Compt. rend.*, 1919, **169**, 62—64).—*cyclopentanone* and *cyclohexanone* and their homologues are readily converted into unsaturated bicyclic ketones when their vapours are passed over calcium hydride. Calcium carbide is not so satisfactory a condensing agent, only giving a good result with *cyclopentanone* out of the four ketones examined. W. G.

Synthesis of Ketimines by Catalytic Methods. GEORGES MIGNONAC (*Compt. rend.*, 1919, **169**, 237—239).—It has been found possible to prepare certain ketimines by passing the vapour of the ketone, along with ammonia, over thorium oxide at 300 — 400° , the temperature varying with the ketone used. This method is not applicable to purely aliphatic ketones, owing to the readiness with which their ketimines undergo condensation. Successful results were obtained with acetophenone, propionophenone, and benzophenone, but only a very small yield was obtained from *cyclohexanone*. W. G.

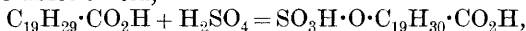
Hydrogenation of Piperonal Ketone and of Dipiperonal Ketone. VAVON and FAILLEBIN (*Compt. rend.*, 1919, **169**, 65—67).—The method with platinum black previously described (compare A., 1914, i, 694) may be used satisfactorily for the hydrogenation of piperonal and dipiperonal ketones. In the latter case, the reaction takes place in two stages, giving first *dihydropiperonal ketone*, $\text{CH}_2 \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{C}_6\text{H}_5 \cdot \text{CH} : \text{CH} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_5 \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{CH}_2$, m. p. 99° , and then the fully saturated *ketone*, $\text{CO}(\text{CH}_2 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_5 \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{CH}_2)_2$, m. p. 55° . Both the yellow and the white forms of piperonal ketone, as described by Haber (compare A., 1891, 704), on hydrogenation give the same saturated *ketone*, m. p. 51° , b. p. $168^{\circ}/13$ mm., giving an *oxime*, m. p. 98° , and a *semicarbazone*, m. p. 166° . The authors consider that the yellow form, m. p. 107° ,

as described by Haber, is but an impure specimen of the white form, m. p. 111°. W. G.

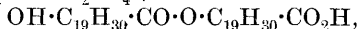
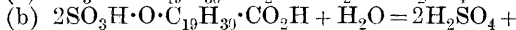
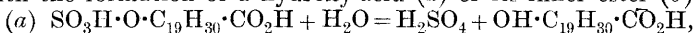
Alcoholysis of Balsams. ERNEST FOURNEAU and MARIO CRESPO (*Bull. Soc. chim.*, 1919, [iv], **25**, 386—389).—The process, which consists in boiling the balsam for six hours with an equal weight of ethyl alcohol containing 3% of hydrogen chloride, neutralising the product with sodium carbonate, and distilling off the esters and alcohols in steam, does not attack the resins. The esters and alcohols are separated by fractional distillation. The results indicate that the balsams are a mixture of cinnamyl and benzyl cinnamates and benzoates in varying proportions, and resins.

W. G.

The Action of Sulphuric Acid on Colophony. AD. GRÜN (*Chem. Umschau Fett. Ind.*, 1919, **26**, 77—79).—When colophony is mixed with light petroleum and treated with sulphuric acid for several hours at -5° , the sulphuric acid combines with the double bond of the abietic acid,



and on boiling the sulphuric acid ester with water, it is decomposed with the formation of a hydroxy-acid (a) or its inner ester (b):



or a mixture of the two products. From the acid value and acetyl value of the product obtained in one experiment, it was calculated that it consisted of 64.1% of the inner ester, 26.5% of unaltered abietic acid, and 9.4% of unsaponifiable matter. Esterification of colophony with sulphuric acid in the presence of methyl alcohol, and decomposition of the product by boiling with water, yields only the methyl ester of abietic acid, with not more than a trace of hydroxy-acid. The methyl ester absorbs only two molecules of halogen when treated with Wijs' iodine chloride solution, whereas the free abietic acid absorbs three molecules. [See also *J. Soc. Chem. Ind.*, 1919, 589A.] C. A. M.

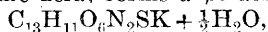
Researches on Chlorophyll. XXV. Phytol. II. RICHARD WILLSTÄTTER, OTTO SCHUPPLI, and ERWIN W. MAYER (*Annalen*, 1919, **418**, 121—147).—The supposed difference between the oxidation products of crude and distilled phytol (compare Willstätter, Mayer, and Hüni, A., 1911, i, 144) is found to be non-existent, α - and β -phytols containing the double linking in the same position. After distillation, phytol does, however, lose water the more readily, especially when heated with phthalic anhydride or acetic acid, probably owing to the existence of two geometrically isomeric forms of the alcohol. The purest preparations of the ketone, obtained by oxidising phytol, have compositions agreeing well with the formula $\text{C}_{15}\text{H}_{30}\text{O}$, but they all contain oxygen-rich admixtures, which are most persistently retained. Repeated conversion of the ketone into its 1-naphthylhydrazine-4-sulphonic acid derivative, followed by

crystallisation and hydrolysis, yields a purified product, the formula of which is most probably $C_{17}H_{34}O$. The action of ozone or chromic acid on this product gives, not a lower ketone, but simply admixtures of increasing oxygen content. The fatty acid occurring with the ketone, and also formed from the latter on oxidation, has not the formula formerly assumed, namely, $C_{14}H_{28}O_2$, but is most probably $C_{16}H_{32}O_2$. Phytol therefore contains the double linking between the third and fourth carbon atoms, and phytenic acid, which is readily converted into an isomeric lactone, should possess the formula $C_{15}H_{31} \cdot CMe \cdot CMe \cdot CO_2H$, since Fichter, Kiefer, and Bernouilli's results (A., 1910, i, 88) show that alkyl groups in the α - and β -positions produce instability of the Δ^1 -acids towards 60% sulphuric acid, being transformed thereby completely into lactones.

The hypothetical structure suggested for phytol by Willstätter, Mayer, and Hüni (*loc. cit.*) thus becomes improbable, the occurrence of derivatives with branched carbon atom chains and of none with normal chains among the oxidation products indicating complex branching of the carbon atom skeleton of phytol.

The purification or isolation of ketones or aldehydes by converting them into derivatives which contain an acidic group, and hence yield salts capable of crystallisation, is illustrated by various examples.

Thus, *methyl-ethyl-ketone-phenylhydrazone-m-carboxylic acid*, $C_{11}H_{14}O_2N_2$, obtained by the action of *m*-hydrazinobenzoic acid on the ketone, crystallises in plates, m. p. 143° . *Methyl-hexyl-ketone-phenylhydrazone-m-carboxylic acid* does not crystallise, but its *ammonium salt*, $C_{15}H_{25}O_2N_3$, crystallises in bundles of leaflets, m. p. 151° . *Methyl-nonyl-ketone-phenylhydrazone-m-carboxylic acid* forms spherical, crystalline aggregates, m. p. 93° , but is unstable; its *ammonium salt*, $C_{18}H_{31}O_2N_3$, crystallises in colourless leaflets, m. p. 146 — 147° (frothing). *Methyl-stearyl-ketone-phenylhydrazone-m-carboxylic acid*, $C_{26}H_{44}O_2N_2$, forms spherical, crystalline nodules, m. p. 83 — 84° (decomp.), and its *ammonium salt*, which crystallises in leaflets, m. p. 136° (decomp.), is, like the compounds described above, converted quantitatively into the ketone by boiling 17% sulphuric acid. *Carvone-phenylhydrazone-m-carboxylic acid*, $C_{17}H_{20}O_2N_2$, separated from commercial carvone mixed with four times its quantity of limonene, forms rhombic plates, m. p. 158° . *Methyl-nonyl-ketone-1-naphthylhydrazone-4-sulphonic acid* gives a crystalline *sodium salt*, m. p. 250 — 252° (decomp.). *Methyl-succinic-acid-1-naphthylhydrazone-4-sulphonic acid*, obtained by hydrolysing the ketone-1-naphthylhydrazone-4-sulphonic acids by means of methylsuccinic acid, forms a *potassium salt*,



which crystallises in yellow leaflets, loses its water of crystallisation at 100 — 110° , and has m. p. 203 — 204° (decomp.).

When treated with potassium 1-naphthylhydrazine-4-sulphonate, the ketone obtained by oxidising phytol by means of either ozone or chromic acid gives a *potassium salt*, $C_{27}H_{41}O_3N_3SK$, which crystallises in slender, white needles sintering at 140° , m. p.

164—165° (decomp.). The ketone yields a semicarbazone, $C_{18}H_{37}ON_3$, m. p. 66·5—67°. The pure ketone, $C_{17}H_{34}O$, obtained by hydrolysis of either the above potassium salt or the semicarbazone, contains 3—4% of the enolic modification, and forms a colourless, mobile liquid, b. p. 175—175·5°/11 mm., D_4^0 0·844, D_4^{20} 0·834, n_D^{20} 1·44516. Its *oxime*, $C_{17}H_{35}ON$, is a colourless, viscous oil, b. p. 201·6—202°/9 mm., D_4^0 0·879. The alcohol, $C_{17}H_{36}O$, obtained by reducing the ketone by means of sodium and alcohol, forms a viscous oil, b. p. 176—177·5°/10 mm., D_4^0 0·847, D_4^{20} 0·837, n_D^{20} 1·45037. When heated with phosphoric oxide, this alcohol gives the olefine, $C_{17}H_{34}$, b. p. 288—291°/719 mm., 153—155·5°/10 mm., D_4^{20} 0·790, which in acetic acid solution is converted by platinum and hydrogen into the corresponding paraffin, $C_{17}H_{36}$, b. p. 161—162°/15 mm., D_4^0 0·794, D_4^{20} 0·780, n_D^{20} 1·43763. This paraffin is not identical with the saturated hydrocarbon previously described as a product of the fractional distillation of the crude ketone. The formation of the hydrocarbon, $C_{15}H_{32}$, b. p. 131—132°/13 mm., 249—250°/718 mm., as a by-product of the hydrolysis of phytol ozonide is confirmed.

The action of ozone on the ketone in ethyl chloride solution yields the peroxide, $C_{17}H_{34}O_2$, as an oil, D_4^0 0·899, D_4^{20} 0·885, with a piercing odour. A considerable part of the oxygen taken up is lost when the peroxide is distilled, even under diminished pressure. It gives an intense reddish-brown coloration with titanium sulphate and liberates iodine, but not in the calculated proportion, from acid or neutral potassium iodide solution. Even the most active reducing agents convert the peroxide, not into the original ketone, but into products containing more oxygen than this; from these products or from the peroxide itself, the pure ketone may, however, be obtained by way of the semicarbazide. Similar behaviour is exhibited by *methyl nonyl ketone peroxide*, $C_{11}H_{22}O_2$, which forms a colourless oil of piercing odour.

The oily, fatty acids formed together with formic acid by oxidising phytol in various ways, by oxidising the ketone, $C_{17}H_{34}O$, by means of either chromic acid or alkaline bromine solution, or by boiling the ozonide of the hydrocarbon, $C_{17}H_{34}$, apparently range in formula from $C_{16}H_{32}O_2$ to $C_6H_{12}O_2$. The ozonide yields also a hydrocarbon, $C_{14}H_{30}$ (?), b. p. 114—117°/11 mm., 241—244°/723 mm., and this, when oxidized, gives a mixture of carboxylic acids and a carbonyl compound, (? ketone), $C_{12}H_{24}O$, which is a mobile liquid, b. p. 84°/14 mm., 188—189°/726 mm., with the odour of lemons, and forms a semicarbazone, m. p. 121—123°.

Fractionation of the acids formed on degradation of the olefine, $C_{17}H_{34}$, and purification by means of the *silver* salt, m. p. 191—193°, gives mainly the acid, $C_{17}H_{32}O_2$, b. p. 201—204°/13 mm., D_4^0 0·901, D_4^{20} 0·887, n_D^{20} 1·44967; the corresponding *amide*, $C_{16}H_{30}ON$, forms leaflets, m. p. 46·5—48·5°.

T. H. P.

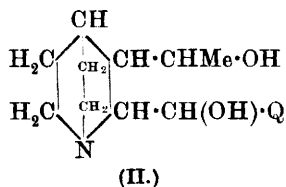
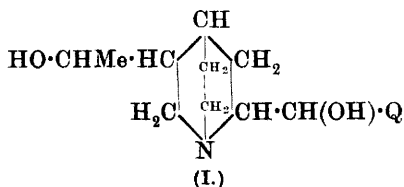
β -Homochelidonine. KANJIRO MOMOYA (*J. Pharm. Soc. Japan*, 1919, No. 444, 110—118 and 6—8).—Protopine and β -homo-

chelidonine, occurring in the alcoholic extract of the roots of *Macleya cordata*, are best separated by means of dilute aqueous ammonia. At 13°, the solubility of protopine in 1% aqueous ammonia is 1.15 grams per litre, whilst that of β -homochelidonine is 6.0 grams per litre. Still further purification is possible through the hydrochlorides; 100 c.c. of water at the ordinary temperature dissolve 14.5 grams of β -homochelidonine hydrochloride, but only 0.7 gram of protopine hydrochloride.

β -Homochelidonine yields two crystalline compounds with methyl iodide, one ($1\text{H}_2\text{O}$), easily soluble, m. p. 198°, the other ($3\text{H}_2\text{O}$), sparingly soluble, m. p. 211°. With methyl sulphate, it yields a *methosulphate* ($3\text{H}_2\text{O}$), m. p. 215°. With mercuric acetate, it yields a new base, *dehydro- β -homochelidonine*, which melts at 136°, re-solidifies, and melts again at 203—204°. It is optically inactive, dissolves in ethyl alcohol and in chloroform, but is sparingly soluble in water. By oxidation with potassium permanganate, it yields *m*-hemipinic acid and an acid, $\text{C}_{11}\text{H}_{11}\text{O}_4\text{N}$, which was not further studied.

CHEMICAL ABSTRACTS.

Cinchonidine. E. LÉGER (*Compt. rend.*, 1919, **169**, 67—70).—With hydrobromic acid (D 1.5), cinchonidine yields *hydrobromo-cinchonidine hydrobromide*, m. p. 95°. When heated for forty-eight hours with 50% sulphuric acid, cinchonidine gives *hydroxy-dihydrocinchonidine*, $\text{C}_{19}\text{H}_{24}\text{O}_2\text{N}_2$, m. p. 242—243° (corr.), $[\alpha]_D - 101.7^\circ$ (in alcohol), giving a *diacetyl* derivative. It is formed by the addition of the elements of water to the grouping $\text{CH}_2\text{:CH}$ to give the grouping $\text{CH}_2\text{-CH(OH)}$. When heated with 70% sulphuric acid at 115° for ten hours, hydroxydihydrocinchonidine yields *apocinchonidine* and β -cinchonidine, thus differing from the oxydihydrocinchonines, which give cinchonigine, cinchoniline, and *apocinchonine*. Based on these observations, the author suggests for hydroxydihydrocinchonidine and α - and β -hydroxydihydrocinchonines the constitutions indicated in formulæ I and II respectively, where Q represents the quinoline residue:

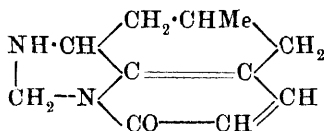


W. G.

Constitution of Cytisine. ERNST SPÄTH (*Monatsh.*, 1919, **40**, 15—33).—The author discusses previous publications on the constitution of cytisine (Partheil, A., 1893, i, 119; 1894, i, 558; 1895, i, 119, 254; Freund and Friedmann, A., 1901, i, 288; Freund, A., 1904, i, 263; Freund and Horkheimer, A., 1906, i, 302), more particularly those of Ewins (T., 1913, **103**, 97) and Freund and Gauff

(*Arch. Pharm.*, 1918, **256**, 33). The author shows (following abstract) that the cytosoline obtained by Freund by the action of hydriodic acid and red phosphorus on cytosine is 2-hydroxy-6:8-dimethylquinoline. As regards the presence or absence of the quinoline ring in the cytosine molecule, the assumption that the pyridine or benzene nucleus of cytosoline arises by extension of a five-membered ring is an improbable one; further, van de Moer's reaction (A., 1891, 946; also Gorter, A., 1896, ii, 344) indicates distinctly the presence of an α -pyridone residue in cytosine. The 6- and 8-methyl groups of cytosoline may exist in the same positions in cytosine, or, as Ewins suggested (*loc. cit.*), that in the 6-position may have arrived by migration during the conversion of cytosine into cytosoline. The oxygen atom most probably occupies corresponding places in the two molecules. In cytosine, the oxygen atom exists in the form of neither hydroxyl, nor normal keto-group, nor as a bridge; the assumption that it occupies the same position as in cytosoline renders probable its occurrence as an acetylaminocarbonyl group, as in α -pyridone. Since cytosine exhibits marked resistance towards reducing agents, the assumption is justified that the two double linkings form a conjugated pair in a single ring.

On the basis of the above considerations, the fourteen possible structures for the cytosine molecule are discussed, the decision in favour of the annexed formula resting on the apparent formation of isovaleric acid by the action of barium permanganate on cytosine; this action is to be investigated further when a larger supply of cytosine is available. The similarity of this structure to that of leucine, which frequently occurs free in the



Papilionaceae, suggests that this amino-acid may be the parent substance of the cytosine.

Van de Moer's reaction is given by a number of derivatives of 2-pyridone, especially with 1-methyl-2-pyridone, and also, though less intensely, with 1-methyl-2-quinolones and 1-methyl-2-hydroxyquinolines. The reaction is also shown by 2-hydroxyquinoline, 2-hydroxy-6-methylquinoline, 2-hydroxy-8-methylquinoline, 2-hydroxy-6:8-dimethylquinoline, 2-keto-1:6-dimethyl-1:2-dihydroquinoline, 2-keto-1:8-dimethyl-1:2-dihydroquinoline, and 2-keto-1:6:8-trimethyl-1:2-dihydroquinoline. Negative results are obtained with hydrocarbostyryl, its 1-methyl derivative, and 4-hydroxyquinoline.

1-Methylhydrocarbostyryl, $\text{C}_9\text{H}_8\text{ONMe}$, prepared from carbostyryl, sodium methoxide, and methyl sulphate, forms an oil, b. p. 165—166°/13 mm., and is difficult to demethylate by means of hydriodic acid.

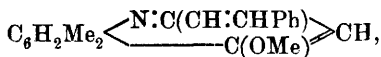
Zerewitinov's method of estimating active hydrogen gives with cytosine an amount of methane corresponding with one atom of active hydrogen, a similar result being obtained with cytosoline.

T. H. P.

Synthesis of Cytisoline. ERNST SPÄTH (*Monatsh.*, 1919, **40**, 93—128).—Cytisoline (Freund, A., 1904, i, 263) is proved to be 2-hydroxy-6:8-dimethylquinoline (compare Ewins, T., 1913, **103**, 97) by the following method. The additive compound obtained by warming 6:8-dimethylquinoline with methyl sulphate is oxidised by potassium ferricyanide and aqueous sodium hydroxide solution to 2-*keto*-1:6:8-*trimethyl*-1:2-*dihydroquinoline*, $C_{12}H_{13}ON$, faintly yellow crystals, m. p. 71—72°, which is converted by phosphorus pentachloride and a little phosphoryl chloride at 135—140° into methyl chloride and 2-*chloro*-6:8-*dimethylquinoline*, long needles, m. p. 56°. The heating should not be prolonged after methyl chloride ceases to be evolved; if it is continued for six hours, the product is a *dichlorodimethylquinoline*, long needles, m. p. 108—109°. 2-Chloro-6:8-dimethylquinoline is converted into 2-hydroxy-6:8-dimethylquinoline by heating with water at 240° for two hours, or, better, with methyl-alcoholic sodium methoxide at 100° for forty-five minutes, the resulting 2-methoxy-6:8-dimethylquinoline being easily converted into 2-hydroxy-6:8-dimethylquinoline by heating with concentrated hydrochloric acid at 210—220° for two hours, or simply by evaporation with hydrochloric acid and subsequent heating on the water-bath.

The identity of 2-hydroxy-6:8-dimethylquinoline, m. p. 201—202°, with cytisoline (m. p. 199°, according to Freund, *loc. cit.*) is shown by the m. p. of the mixture, 200—201°, by the conversion of each into identical chloro-, methoxy-, nitro-, and tetrahydro-derivatives, and by the formation of cytisinic acid from each by oxidation with chromic and acetic acids.

Other substances were examined in the course of the investigation. 4-*Hydroxy*-6:8-*dimethylquinoline*, needles, m. p. 221°, softening at 219°, was obtained as follows. 4-*Hydroxy*-2:6:8-*trimethylquinoline*, m. p. 263—264°, prepared from *m*-4-xylidine and ethyl acetoacetate by Conrad and Limpach's method, was converted in warm methyl-alcoholic solution by methyl sulphate and sodium hydroxide into 4-*methoxy*-2:6:8-*trimethylquinoline*, pearly leaflets, m. p. 111—112°, which is much more difficultly hydrolysed by hydrochloric acid than are the 2-methoxyquinolines. It reacted with benzaldehyde at 135—140° in the presence of zinc chloride to form 4-*methoxy*-2-*styryl*-6:8-*dimethylquinoline*,



trichroic needles, m. p. 137—138°, which in glacial acetic acid solution containing a little concentrated sulphuric acid was oxidised by potassium permanganate solution, yielding a quinolinecarboxylic acid. This was not isolated in the pure state, but was converted by evaporation with concentrated hydrochloric acid into 4-*hydroxy*-6:8-*dimethylquinoline-2-carboxylic acid*, m. p. 250° (decomp.), from which 4-hydroxy-6:8-dimethylquinoline was obtained by heating in a vacuum at 260—280°. The last compound yielded 6:8-dimethylquinoline by distillation with zinc dust, and thus the proof

was furnished that the methyl group in position 2 in 4-methoxy-2:6:8-trimethylquinoline entered into reaction with benzaldehyde.

2-Hydroxy-6-methylquinoline, needles, m. p. 232—233°, and *2-hydroxy-8-methylquinoline*, needles, m. p. 219—220°, were prepared from 6-methylquinoline and 8-methylquinoline respectively in the same way as 2-hydroxy-6:8-dimethylquinoline above; the intermediate compounds are, in the first case, *2-keto-1:6-dimethyl-1:2-dihydroquinoline*, crystals, m. p. 84—85°, *2-chloro-6-methylquinoline*, needles, m. p. 114—115°, and *2-methoxy-6-methylquinoline*, m. p. 63°, and, in the second case, *2-keto-1:8-dimethyl-1:2-dihydroquinoline*, m. p. 92—93°, b. p. 198—198.5°/13 mm., *2-chloro-8-methylquinoline*, needles, m. p. 60—61°, and *2-methoxy-8-methylquinoline*, b. p. 142—143°/18 mm. C. S.

Harmine and Harmaline. III. and IV. WILLIAM HENRY PERKIN, jun., and ROBERT ROBINSON (T., 1919, 115, 933—967; 967—972).

An Anomaly in the Solubility of Sparteine. A. VALEUR (*Bull. sci. pharmacol.*, 1919, 26, 145—151).—Mixing aqueous solutions of sodium carbonate and sparteine sulphate results in a slight turbidity, separation of supernatant oily layer, or complete transparency, depending on concentration and temperature. Increase in temperature causes decreased solubility, attributed to the abnormal solubility of basic sparteine sulphate, produced by the action of sodium carbonate on the neutral sulphate. Sparteine alone shows abnormality; 0.496% solution becomes turbid at 12.5°, 0.18% solution at 50°. Solutions of 0.13% or lower do not develop turbidity at the b. p. The solubility is decreased by sodium carbonate, thus in 5% solution, a 0.03% solution of sparteine becomes turbid on boiling. Using progressively regularly increasing amounts of pure sparteine ($[\alpha]_D^{20} 46'$) in 5% sodium carbonate, the author found that the temperature at which the solutions began to become turbid was regularly decreased by 2.5° with each increase in 0.01% of sparteine in concentrations between 0.09% and 0.18%, the temperatures ranging between 47.5° and 25°. Above or below these temperatures, irregularities appeared. A curve is presented. Variations in the strength of the carbonate solution caused appropriate variations in the general level of the curves, although they were found to run parallel to that obtained with the 5% sodium carbonate solution. The method consisted in placing the sample in a test-tube with thermometer in a water-bath and observing the exact temperature of the appearing turbidity. It was necessary to work with carefully filtered solutions, to use either a new tube for each test, or to wash the tube with acid, water, and the new solution to be tested. Wide discrepancies of earlier results as to the solubility are due to lack of appreciation of the effect of temperature changes. The author prepared a solution of sparteine sulphate by adding an excess to water at 10.8°, keeping for two days, centrifuging, and filtering, and he determined the solubility by titration

with 0.1*N*-hydrochloric acid, using methyl-orange, by precipitation with silicotungstic acid, by precipitation with picric acid, and by observing the temperature of appearing turbidity in 5% sodium carbonate. The results coincide, and give about 0.32% as the solubility of the compound at 22°. CHEMICAL ABSTRACTS.

Constitution of the Dialkyltetrahydrodipyridyls. BRUNO EMMERT (*Ber.*, 1919, **52**, [B], 1351—1353).—It was observed by Hofmann (A., 1881, 921) that unstable, dialkyltetrahydrodipyridyls are formed by the action of sodium amalgam on alkylpyridinium haloids, and it was assumed that the pyridine nuclei were united in the α -position. The author has obtained similar substances by the electrolysis of alkylpyridinium salts and by the action of water on sodium pyridine (A., 1909, i, 602; 1917, i, 221), and has therefore endeavoured to deduce their composition with greater certainty. Attempts to reduce *NN'*-dibenzyltetrahydrodipyridyl to the corresponding dipiperidyl were unsuccessful by reason of the tendency of the substance to resinify, but, on distillation with zinc dust, toluene and 4:4'-dipyridyl were obtained. The presence of 2:2'-dipyridyl could not be detected, so that, contrary to Hofmann's assumption, the pyridine nuclei in such compounds are united in the 4-position. H. W.

Isomerism among Derivatives of Indazole. K. VON AUWERS (*Ber.*, 1919, **52**, [B], 1330—1339).—The recent communications of Harries (this vol., i, 131) and Freund and Kessler (this vol., i, 283) on isomerisation among heterocyclic bases have induced the author to publish a preliminary account of investigations of a similar nature which are being carried out in his laboratory.

1-Acetylandazole, $C_6H_4 \begin{smallmatrix} \text{CH} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} \text{Ac}$, is prepared by the Beckmann transformation of *o*-aminobenzaldoxime, but the yields in different experiments vary greatly; it has m. p. 169—171°, b. p. 191°/15 mm. (slight decomp.). The sparingly soluble *nitrate* crystallises in small, shining needles grouped in rosettes, whilst the *compound* with mercuric chloride forms flat, shining needles. 1-Acetylandazole is readily converted by alkali hydroxide or by boiling water into the *N*-acetyl derivative of *o*-aminobenzaldoxime or into the oxime itself. 2-Acetylandazole, $C_6H_4 \begin{smallmatrix} \text{CH} \\ \diagdown \quad \diagup \\ \text{N} \end{smallmatrix} \text{Ac}$, exists in two forms.

The stable modification, long, transparent, oblique prisms, m. p. 42—43°, b. p. 260°, is formed by the action of acetic anhydride on indazole, and is rapidly hydrolysed by warm acids or alkali hydroxides; it yields a double *compound* with mercuric chloride. The labile *modification* crystallises in needles or plates, m. p. 106°, and is prepared by the action of acetyl chloride on an ethereal suspension of the silver salt of indazole or by acetylation of indazole with acetyl chloride in the presence of pyridine. It is converted into the stable derivative, m. p. 42°, when distilled under diminished

pressure, by crystallisation from solvents of moderately high boiling point, and, slowly, at the ordinary temperature.

The *N*-alkylindazoles have been investigated by Fischer and Tafel (A., 1885, 541), who prepared the 2-alkyl derivative by heating indazole with alkyl iodides. When, however, indazole is heated with alkyl iodides and sodium in the presence of methyl or ethyl alcohol, mixtures of 1- and 2-alkylindazoles are obtained, which are most conveniently separated by fractional distillation followed by crystallisation of the individual fractions, or, when this is not possible, by means of the picrates. The course of the reaction is deduced from a study of the action of ethyl iodide, sodium, and ethyl alcohol on 3-methylindazole, whereby a mixture of 3-methyl-1-ethylindazole, b. p. 245.5° (m. p. of picrate, 190—192° or 192—194°, according to the rate of heating), and 3-methyl-2-ethylindazole, b. p. 284—285° (m. p. of picrate, 212—213°), is obtained, the products being identical with those described by Fischer and Tafel (*loc. cit.*).
H. W.

Alkyl Derivatives of Indazole-3-carboxylic Acid. K. von AUWERS and R. DERESER (*Ber.*, 1919, 52, [B], 1340—1351).—The action of various alkylating agents on indazole-3-carboxylic acid and its esters has been investigated. The behaviour is more complex than that of indazole itself (preceding abstract). Fortunately, the widely differing ease of esterification of the alkylindazolecarboxylic acids affords both a means of fixing their constitution and also of separating mixtures of them into their components. Thus indazole-3-carboxylic acid is readily esterified by the Fischer-Speier process, and this is true of one of the alkylated acids, which is thus a 1-alkyl derivative, whereas the second acid, which can only be esterified with difficulty, must be the 2-alkyl compound. The esters of 2-alkylindazole-3-carboxylic acid are obtained by the action of alkyl iodides on the silver salt of the acid or on the silver compound of the ester.

Direct alkylation of indazole-3-carboxylic acid with alkyl iodide is not a suitable method, since the substances scarcely react at 100°, whilst at higher temperatures compounds containing iodine result. The method may, however, be applied to the esters; thus methyl indazole-3-carboxylate and methyl iodide at 100° yield a mixture of methyl 2-methylindazole-3-carboxylate and the corresponding acid (formed by the action of the liberated hydrogen iodide); the ethyl ester does not react with ethyl iodide under similar conditions.

2-Alkylindazole-3-carboxylic acids are readily obtained by the action of methyl or ethyl sulphate and sodium hydroxide on indazole-3-carboxylic acid, the 1-alkyl isomerides either not being formed at all or in very small amount. The methyl ester, when similarly treated, yields, however, a mixture of the 1- and 2-methyl derivatives. Methyl indazole-3-carboxylate is converted by diazomethane exclusively into the 2-methyl compound.

Alkylation with sodium alkoxide and alkyl iodide leads, in general, to a mixture of isomerides, the relative proportions of

which vary with the particular ester used and also with the alkyl iodide.

The esters of indazole-3-carboxylic acid and its homologues can be distilled without undergoing decomposition, whilst the corresponding free acids eliminate carbon dioxide when heated and yield the indazoles; with the 1-alkyl acids, this happens at the melting point, with the 2-alkyl acids, however, at a higher temperature.

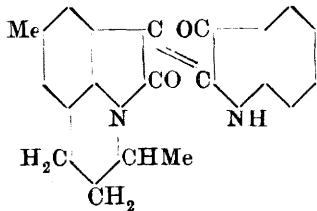
The following individual compounds are described: indazole-3-carboxylic acid, m. p. 260—261°; methyl ester, m. p. 168—169°; ethyl ester, yellow, shining needles, m. p. 136—137°; 2-methylindazole-3-carboxylic acid, m. p. 224—225° (decomp.); methyl ester, yellow crystals, m. p. 61—62°; 2-ethylindazole-3-carboxylic acid, small leaflets, m. p. 180—181°; ethyl ester, slender needles, m. p. 47—48°, b. p. 179—181°/11 mm.; 1-methylindazole-3-carboxylic acid, slender needles, m. p. 213—214°; methyl ester, colourless needles, m. p. 75—77°; 1-ethylindazole-3-carboxylic acid, glassy needles, m. p. 162—163°; ethyl ester, b. p. 190—192°/10 mm.

H. W.

The Indirubins. JH. MARTINET (*Compt. rend.*, 1919, 169, 183—185).—The author has prepared a number of substituted indirubins by three different processes, namely, (1) condensation of the isatins with indoxyl-ic acid in slightly alkaline medium in an atmosphere of hydrogen; (2) condensation of the same isatins with 2-anilinoisatin in ammoniacal solution in a current of hydrogen sulphide; by this method, a large part of the product often remains in the mother liquor as a leuco-base, in which case, after filtration, these liquors should be warmed in a current of air; (3) very easily by adding to an acetic acid solution of the isatin, warmed on a water-bath, the technical fusion of phenylglycine.

The following indirubins have been prepared:

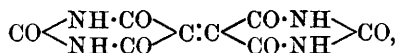
From isatin, indirubin itself; from 1-methylisatin, 2-indoxyl-1-methylindole; from 5-bromo-1-methylisatin, 2-indoxyl-3-(5-bromo-1-methyl)indole, m. p. 265—266°; from 1-ethylisatin, 2-indoxyl-3-(1-ethyl)indole; from 5-bromo-1-ethylisatin, 2-indoxyl-3-(5-bromo-1-ethyl)indole, m. p. 250—251°; from 5-methylisatin, 2-indoxyl-3-(5-methyl)indole, m. p. 289°; from 5:7-dimethylisatin, 2-indoxyl-3-(5:7-dimethyl)indole, m. p. 337°; from 1:7-trimethyleneisatin, 2-indoxyl-3-(1:7-trimethylene)indole, m. p. 252°; from 5-methyl-1:7-trimethyleneisatin, 2-indoxyl-3-(5-methyl-1:7-trimethylene)indole, m. p. 265°; from 5-methyl-1:7- α -methyltrimethyleneisatin, 2-indoxyl-3-(5-methyl-1:7- α -methyltrimethylene)indole (annexed formula), m. p. 204—205°.



All of these substances are obtained as slender, brownish-violet needles. They give violet-red, alcoholic solutions, the colour of which is rapidly removed on warming with a few drops of potassium hydroxide in the case of those indirubins which have a sub-

stituent attached to nitrogen. [See, further, *J. Soc. Chem. Ind.*, September.] W. G.

Hydurilic Acid and s-Dimethylhydurilic Acid. HEINRICH BILTZ and MYRON HEYN (*Ber.*, 1919, **52**, [B], 1298—1316).—Hydurilic acid is conveniently prepared by the action of heat on dialuric acid, conversion of the crude product into 5-bromo-5-ethoxyhydurilic acid, and reduction of the latter with stannous chloride. It is also readily obtained by oxidation of barbituric acid in aqueous solution with potassium permanganate, but is not formed from an acid solution. Hydurilic acid is itself further oxidised by permanganate, probably to 5-hydroxyhydurilic acid; the product, however, could not be adequately purified, and, further, could not be reduced to hydurilic acid. 5-Methoxyhydurilic acid is readily obtained by the gentle reduction of 5-bromo-5-methoxyhydurilic acid (Biltz, Heyn, and Hamburger, *A.*, 1916, i, 507) by potassium iodide or sodium sulphite, whilst more powerful reducing agents yield hydurilic acid; it forms coarse, hexagonal platelets, which soften at 170° and decompose at 230—240°. With bromine and water, it re-forms bromomethoxyhydurilic acid, whilst with chlorine it gives 5:5'-dichlorohydurilic acid. 5-Ethoxyhydurilic acid, prepared in a similar manner, crystallises in pyramids or double pyramids, which decompose at about 242° after becoming red at about 210°. The alkyloxyhydurilic acids are powerful acids; *potassium methoxyhydurilate*, rectangular platelets, is described. The alkyloxy-acids eliminate alcohol when heated, and yield *dehydrohydurilic acid*,



which could not be crystallised without change and which decomposes at about 250°; it appears to be converted in aqueous solution into 5-hydroxyhydurilic acid. The solid acid (but not the aqueous solution) is reduced by potassium iodide to hydurilic acid. With methyl alcohol, chlorine, and bromine, respectively, it yields 5-methoxyhydurilic acid, 5:5'-dichlorohydurilic acid, and 5:5'-dibromohydurilic acid, long, four-sided prisms which evolve bromine at 110° and decompose at 160°. When heated at 120°, the dibromo-acid yields dehydrohydurilic acid, thus exactly resembling 5:5'-dibromotetramethylhydurilic acid; with alcohols, it gives 5-alkyloxyhydurilic acids, whilst dilute aqueous ammonia converts it into 5-aminohydurilic acid, leaflets, decomposing from 70°; the latter is reduced by stannous chloride to uramil and barbituric acid. It reacts with potassium cyanate and molten carbamide, without, however, yielding crystallisable substances. Solid dehydrohydurilic acid also reacts with an aqueous solution of carbamide, giving a *substance*, rectangular platelets, m. p. about 140° (decomp.) after softening at 130°.

5-Methoxy- and 5-ethoxy-tetramethylhydurilic acids are more conveniently prepared by the reduction of 5-bromo-5-methoxy- or

5-bromo-5-ethoxy-tetramethylhydurilic acids with potassium iodide than by the process previously described (*loc. cit.*); tetramethyl-dehydrohydurilic acid readily reacts with chlorine to yield 5:5'-dichlorotetramethylhydurilic acid.

Unsuccessful attempts are described to prepare a monomethylhydurilic acid by the action of heat on methylalloxantin; the product, however, was hydurilic acid. Similarly, diethylbarbituric acid was found not to condense with dialuric acid.

[In part, with H. BÜLOW.]—*s*-Dimethylhydurilic acid, rhombic platelets, which decompose at 306—308° after darkening at 270°, is prepared by heating *s*-dimethylalloxantin at 150°, and is conveniently purified through 5-bromo-5-methoxydimethylhydurilic acid, which decomposes at 235—240° after softening at about 225°. It is converted by methyl sulphate into tetramethylhydurilic acid. 5-Bromo-5'-ethoxydimethylhydurilic acid forms rhombic platelets decomposing at 206—207°. 5-Methoxydimethylhydurilic acid, rectangular platelets, decomposing at 155° after softening at 150°, and 5-ethoxydimethylhydurilic acid, rectangular leaflets, which decompose above 300°, are prepared by the reduction of the corresponding bromo-acids with sodium sulphite. The former, when heated under diminished pressure at 150°, gives crude dimethyl-dehydrohydurilic acid, which, however, could not be purified; on reduction, it yields dimethylhydurilic acid, whilst bromine transforms it into 5:5'-dibromodimethylhydurilic acid, which loses bromine at 80°. 5:5'-Dichlorodimethylhydurilic acid is obtained by the action of hydrochloric acid and potassium chlorate on dimethylhydurilic acid; it forms rhombic platelets, which decompose at 295—300° after becoming discoloured from 270°. H. W.

Formation of Cyanic Acid by Oxidation of Organic Substances. Its Identification Based on Quantitative Analysis. R. FOSSE (*Compt. rend.*, 1919, 169, 91—93).—The presence of cyanic acid in solutions of proteins, alone or with dextrose present, and in ammoniacal solutions of amino-acids, glycerol, carbohydrates, or formaldehyde, after oxidation, is shown by isolating it as its silver salt and analysing this salt. The solution after the oxidation is almost completely neutralised with nitric acid and silver nitrate is added. The precipitate is collected at the pump, washed, and extracted with hot water. On cooling the hot extract, the silver cyanate crystallises out, and may be collected and dried. The salt is heated on a water-bath for one hour in ammoniacal solution with ammonium chloride, after which the solution is acidified with acetic acid and the silver chloride is collected on a Gooch crucible and weighed. The carbamide present in the filtrate is estimated by the usual method. W. G.

Ultramicroscopy of Egg-albumin. J. F. MCCLENDON and H. J. PRENDERGAST (*J. Biol. Chem.*, 1919, 38, 549).—A saturated solution of carefully purified crystalline egg-albumin in distilled

water had a p_H about 4.2, and the ultramicroscope showed only an occasional submicron. On bringing it to $p_H=4.8$ and re-examining it by the microscope, there was a slight increase in the number of submicrons. This points to the protein existing in true solution, and it is remarked that it seems unfortunate that clear solutions of protein should be classed with suspensoids under the term "colloids."

J. C. D.

The Nomenclature of Blood Pigment and its Derivatives.

WILLIAM DOBINSON HALLIBURTON and OTTO ROSENHEIM (*Biochem. J.*, 1919, **13**, 195—198).—Attention is drawn to the unsatisfactory system of nomenclature of the blood pigments and their derivatives introduced by Hoppe Seyler. As an entirely new system would confuse the literature, it is suggested that a considerable simplification of that at present in use would be effected by the deletion of the ill-chosen name hæmochromogen. It is pointed out that this substance is without doubt identical with reduced hæmatin (Stokes, *Proc. Roy. Soc.*, 1864, **13**, 353). The substance hitherto termed hæmatin should be called oxyhæmatin. This small change renders it possible to show the relationship of the blood pigments and their derivatives by means of a very simple table.

J. C. D.

The Effect of Alcohol on the Digestion of Fibrin and Caseinogen by Trypsin. EDWARD STAFFORD EDIE (*Biochem. J.*, 1919, **13**, 219—225).—The action of trypsin on fibrin and on caseinogen is affected by dilute alcohol to such different degrees that it is reasonable to suppose either that there are two enzymes concerned in the digestion of these proteins or that different groups of the same enzyme molecule take part in the hydrolysis of the different proteins.

J. C. D.

Additive Compounds of the Halogen Acids with Diphenylarsinic Acid. V. GRIGNARD and G. RIVAT (*Compt. rend.*, 1919, **169**, 126—129).—When diphenylarsinic acid is dissolved in hydrochloric acid (D 1.17) and the solution allowed to cool, the *hydrochloride*, $\text{AsPh}_2\text{O}\cdot\text{OH}\cdot\text{HCl}$, m. p. 134° , is obtained, but if the acid is first diluted with two volumes of water, the *hydrochloride*, $2\text{AsPh}_2\text{O}\cdot\text{OH}\cdot\text{HCl}$, m. p. $111\text{—}111.5^\circ$, is obtained. The first hydrochloride may be converted into the second by warming it in chloroform with an equimolecular proportion of diphenylarsinic acid, whilst the reverse process is brought about by dissolving the second hydrochloride in hydrochloric acid (D 1.17). In a similar manner, two *hydrobromides*, the one, $\text{AsPh}_2\text{O}\cdot\text{OH}\cdot\text{HBr}$, m. p. $126\text{—}126.5^\circ$, the other, $2\text{AsPh}_2\text{O}\cdot\text{OH}\cdot\text{HBr}$, m. p. $119.5\text{—}120^\circ$, have been obtained. The hydrobromides are less stable than the hydrochlorides.

[By CH. MAUGUIN.]—The crystallographic measurements for these addition compounds, all of which crystallise in the monoclinic system, are: the hydrochloride, $\text{AsPh}_2\text{O}\cdot\text{OH}\cdot\text{HCl}$, has $a:b:c=$

0·8063:1:?, $\beta=109^{\circ}25'$; the hydrochloride, $2\text{AsPh}_2\text{O}\cdot\text{OH}, \text{HCl}$, has
 $\alpha:b:c=0\cdot6346:1:0\cdot801$, $\beta=94^{\circ}30'$; the hydrobromide,

$\text{AsPh}_2\text{O}\cdot\text{OH}, \text{HBr}$,

has $\alpha:b:c=0\cdot790:1:?$, $\beta=108^{\circ}26'$; the hydrobromide,

$2\text{AsPh}_2\text{O}\cdot\text{OH}, \text{HBr}$,

has $\alpha:b:c=0\cdot6333:1:0\cdot779$, $\beta=93^{\circ}56'$.

W. G

Physiological Chemistry.

Relation between the Electric State of the Cell Wall and its Permeability to a Given Ion. PIERRE GIRARD (*Compt. rend.*, 1919, **169**, 94—97).—The author has shown that, by modifying the charge on the cell wall in the case of blood corpuscles, its permeability to chlorine ions is also modified. In suspension in 0.9% sodium chloride solution, the corpuscles neither absorb nor emit chlorine, but in a similar solution acidified with lactic acid, taking into account the expansion of the corpuscles, it is shown that chlorine passes in, due to the electrification of the cell wall by the hydrogen ions of the acid. This positive charge induced by the hydrogen ions on the cell walls is partly annulled if the acid used has a high valency, as is shown by replacing the lactic acid with citric acid. The presence in the sodium chloride solution of a non-toxic, alkaline salt, such as potassium carbonate, tends to increase the negative charge on the cell wall, and chlorine, instead of passing into the cell, passes out. W. G.

Effect of Diet on the Alkaline Reserve of the Blood. J. F. McCLENDON, L. VON MEYSENBUG, O. J. ENGSTRAND, and FRANCES KING (*J. Biol. Chem.*, 1919, **38**, 539—548).—The alkaline reserve in man and the dog appears to be very resistant to the influence of the diet. In the case of the rabbit, however, changes due to diet or starvation were noted. J. C. D.

The Action of Ultraviolet Rays on the Accessory Food Factors. SYLVESTER SOLOMON ZILVA (*Biochem. J.*, 1919, **13**, 164—171).—The accessory food factor present in butter is inactivated by exposure to ultraviolet light for eight hours. This treatment also bleaches the butter and renders it quite unfit for consumption. The antineuritic and antiscorbutic vitamins are not destroyed by ultraviolet rays. J. C. D.

Relationship of the Pancreatic Enzymes. FREDERIC FENGER and MARY HULL (*J. Biol. Chem.*, 1919, **38**, 487—500).—The normal pancreas as removed from the animal is of distinctly acid reaction and possesses high diastatic, considerable lipolytic, and

some proteolytic activity. The first-named enzyme is present in fully activated form, but increased lipolytic activity and proteolytic activity are obtained by the addition of bile and duodenal mucosa respectively. By the addition of adequate amounts of these two substances, it is possible to produce and maintain maximum activity of the three enzymes in the removed pancreas. J. C. D.

The Colours of Colloids. VII. Blue Feathers. WILDER D. BANCROFT (*J. Phys. Chem.*, 1919, **23**, 365—414. Compare this vol., i, 421).—The colours in feathers fall into three categories. Of these, only black, brown, reddish-orange, and yellow are objective chemical colours directly produced by pigment. A second type is structural, notably blue and violet, which are produced by finely divided air bubbles in a specially constructed, transparent layer of thick-walled "box cells" lying below the epidermal cells, which behave in a manner similar to the dust in the atmosphere, and the effect of which is intensified by a brownish-black pigment layer behind. Lastly, there are colours which depend entirely on the position of the light and eye, which are produced by a transparent sheath which acts like a prism. The combination of the structural blue with a yellow pigment gives a structural green. By displacing the air in the "box cells" with a medium of the same refractive index as the cell wall, such as Canada balsam or benzene, the structural blue colour disappears. G. F. M.

The Non-protein Nitrogenous Constituents of Cow's Milk. W. DENIS and A. S. MINOT (*J. Biol. Chem.*, 1919, **38**, 453—458).—Analyses of the total non-protein nitrogen, amino-nitrogen, urea, uric acid, creatine, and creatinine in cow's milk are given. The content of the first three is influenced by the character of the food, being increased in high protein feeding. High figures for these fractions are also found for colostrum. J. C. D.

The Peroxydases in Milk. H. VIOLE (*Compt. rend.*, 1919, **169**, 248—250).—It is shown from an examination of the mammary glands of guinea-pigs that the peroxydase is contained in the glandular cells, and in the case of a healthy mammal, therefore, not submitted to violent treatment, the fresh milk may contain little or no peroxydase. On the other hand, the milk coming from an animal having any affection of the mammary gland may be rich in peroxydase. Similarly, milk which has been heated at 78—80°, and in which, therefore, the peroxydase has been destroyed, may have the latter restored by the addition of fresh organic tissues or liquids of animal or vegetable origin containing them. The peroxydase test is not therefore trustworthy as a means of distinguishing between fresh and heated milk. W. G.

Mechanism of the Toxic Action of Urease. P. CARNOT and P. GÉRARD (*Compt. rend.*, 1919, **169**, 88—90. Compare *Compt. rend. Soc. Biol.*, 1919, April).—The toxicity of soya flour when

injected intravenously or subcutaneously is shown to be due to the action of the urease present in it. In the case of dogs receiving an intravenous injection, it was found that the carbamide present in the blood disappeared very rapidly, although in some cases it reappeared later. The ammoniacal nitrogen content of the blood and organs increased progressively. The phenomena of cerebral intoxication are due to the localisation of ammonia in the brain, this being produced by the action of the urease on the carbamide of the blood and tissues.

W. G.

Chemistry of Vegetable Physiology and Agriculture.

The Preparation of Silica Jelly for Use as a Bacteriological Medium. ALBERT T. LEGG (*Biochem. J.*, 1919, **13**, 107—110).—The success of the method depends on the use of a rather thick collodion dialysing membrane of low permeability, a sufficiently long period being given for the sodium silicate and hydrochloric acid to react after mixing, and the use of distilled water for dialysing. When the product is to be used for culture purposes, it is advisable that tubing and autoclaving should follow immediately after dialysing. J. C. D.

The Vitamine Requirement of Yeast. A Simple Biological Test for Vitamine. ROGER J. WILLIAMS (*J. Biol. Chem.*, 1919, **38**, 465—486).—Attempts to grow pure cultures of yeast in synthetic media from a single cell failed, a finding which recalled the experiments of Pasteur and of Wildiers ("La Cellule," 1901). Further experimentation largely confirmed Wildiers' results, and the possibility of the substance termed "bios" by that author being identical with the water-soluble *B*-vitamine presented itself. It was found that the substance which stimulates the growth of yeast occurs in many of the materials which are known to be sources of water-soluble *B*, and, moreover, the properties of the two substances showed close resemblance. The former substance was not identified as any one of the amino-acids obtained from caseinogen. It is believed that there is justification for concluding that the two substances, Wildiers' "bios" and the so-called water-soluble *B*, are identical. J. C. D.

Preparation of Glycerol by Fermentation. W. CONNSTEIN and K. LÜDECKE (*Ber.*, 1919, **52**, [B], 1385—1391).—The experiments were undertaken with the object of providing the Central Powers with a means of obtaining glycerol after the importation of fats had been prevented by the blockade.

Glycerol is formed to the extent of about 3% in the ordinary

fermentation of sugar, and the yield is considerably increased when fermentation is effected in the presence of slightly alkaline salts, which do not poison the yeast. In these circumstances, however, the solutions are very liable to infection, thereby decreasing the yield of glycerol; in this connexion, sodium sulphite is very useful, since, particularly at high concentrations, it has an antiseptic action and especially hinders the development of the lactic acid bacilli, whilst also it gives the highest yields of glycerol. The latter vary from 23.1% when the weight of sulphite used is 40% of that of the sugar to 36.7% with twice the weight of the sugar; too large an addition of sodium sulphite causes fermentation to be too slow or damages the yeast. The process does not appear to depend on the particular variety of fermentable sugar (refined sugar, crude sugar, or molasses can be used) or on the species of yeast. The latter, which does not increase to more than a slight extent during the sulphite fermentation, can be utilised for further experiments after subjection to a "purification fermentation" in slightly acid solution. The glycerol, after suitable purification, is adapted not only to nitration, but also to pharmaceutical purposes; occasionally it contains small amounts of trimethyleneglycol, probably due to secondary decomposition of glycerol by bacteria.

The volatile products of the fermentation consist chiefly of ethyl alcohol and acetaldehyde. Increase in the quantity of sulphite diminishes the production of alcohol and carbon dioxide and increases that of glycerol and acetaldehyde.

With regard to the mechanism of the reaction, two factors appear to be involved, a general action of salts and a specific sulphite action. Increased production of glycerol occurs in the presence of considerable quantities, not only of slightly alkaline salts, but also of certain neutral or acid salts (calcium chloride, ammonium chloride, sodium chloride, sulphate or nitrate, ferrous sulphate, aluminium sulphate). The specific action of the sulphite is possibly connected with its relationship to aldehydes. H. W.

The Vegetable Proteases. I. Introductory. ERNEST ARTHUR FISHER (*Biochem. J.*, 1919, **13**, 124—134).—The presence of proteinoclastic and peptoclastic enzymes in a number of green plants (cereals in the grass stage, leguminous plants, buckwheat, and white mustard) has been established. A detailed examination of beans, field peas, and buckwheat indicated that all parts of the plant are active in this respect at all stages of growth. The proteinoclastic and peptoclastic action of the leaves increases with increasing maturity, and does not fall off after the flowering stage. There is a distinct increase in the activity of these enzymes after germination. The suggestion is advanced that the peptoclastic action of green fodder plants is sufficiently great to be of assistance to the animal organism in the digestion of the simple protein substances. J. C. D.

Organic Chemistry.

Manufacture of Amyl Acetate and its Homologues from Chloro-hydrocarbons of the Paraffin Series. G. G. OBERFELL and H. T. BOYD (U.S. Pat. 1302583; from *J. Soc. Chem. Ind.*, 1919, **38**, 554A).—Chloro-paraffins are converted into acetic esters by treatment with an alkali acetate and acetic acid in presence of an alkali sulphate. G. F. M.

The Insecticidal Principle of *Chrysanthemum cinerarii-folium* (Insect Powder). RYŌ YAMAMOTO (*Ber. Ōhara Inst. landw. Forsch.*, 1918, **1**, 389—398).—A yellow, viscous oil having powerful insecticidal properties was isolated from the powdered flowers of *Chrysanthemum cinerarii-folium*, the yield being 0.8%. The oil had a saponification number of 216 and an iodine number of 116; from the saponified substance, two alcohols having the formulæ $C_{21}H_{34}O$, m. p. 199° , and $C_{27}H_{46}O$, m. p. 175 — 179° , and two fatty acids having the formulæ $C_{10}H_{18}O_2$ and $C_{16}H_{32}O_2$ (palmitic), were separated. The insecticidal power of the oil was reduced when the oil was heated at 100° or exposed to air for a long period. W. P. S.

Action of Methyl Sulphate and Methyl Alkali Sulphate on Dry Alkali Chlorides and Bromides. J. GUYOT and L. J. SIMON (*Compt. rend.*, 1919, **169**, 435—437).—When methyl sulphate is heated with sodium chloride, reaction at first appears to take place according to the equation $Me_2SO_4 + NaCl = NaMeSO_4 + MeCl$, and is followed by a reaction shown by the equation $2NaMeSO_4 = Na_2S_2O_7 + OMe_2$. The residue, however, always contains normal sodium sulphate, and the quantities of the two gases formed are not theoretical; methyl chloride is in excess. If equimolecular quantities of methyl sulphate and potassium chloride are heated together, two-thirds of the methyl sulphate reacts according to the second of the above equations, the remainder reacting with the potassium chloride, $KMeSO_4 + KCl = K_2SO_4 + MeCl$. If two molecules of potassium chloride are used, the latter reaction disappears almost completely, and the reaction is represented by the equation $2Me_2SO_4 + 2KCl = 2MeCl + OMe_2 + K_2S_2O_7$. Bromides behave in a similar way to chlorides in the reactions. W. P. S.

Interaction between Methyl Sulphate and Chloro-sulphonic Acid. CH. BOULIN and L. J. SIMON (*Compt. rend.*, 1919, **169**, 338—341).—Equimolecular proportions of methyl sulphate and chlorosulphonic acid slowly react according to the equation $SO_2(OMe)_2 + SO_2Cl \cdot OH \rightleftharpoons SO_2Cl \cdot OMe + SO_2(OH) \cdot OMe$,

an equilibrium being reached at the end of a month, when the reaction has proceeded to the extent of 36% to the right. If kept for a further period, a change in acidity slowly occurs, owing to the formation of sulphuric acid, according to the equation $\text{SO}_2(\text{OH})\cdot\text{OMe} + \text{SO}_2\text{Cl}\cdot\text{OH} \rightleftharpoons \text{SO}_2\text{Cl}\cdot\text{OMe} + \text{H}_2\text{SO}_4$; this change at the end of 138 days has not quite reached equilibrium. When, on the other hand, the reaction mixture is subjected to vacuum distillation, the two initial materials practically disappear, and a yield of 50% of methyl chlorosulphonate is obtained, together with small quantities of hydrogen chloride, methyl chloride, and a residue of sulphuric acid. G. F. M.

Wax of a South Brazilian Wild Bee. J. GADAMER (*Arch. Pharm.*, 1917, **255**, 425—441).—The characters and composition of wax produced by a wild bee, probably of the species *Melipona* or *Trigona*, are described. [See *J. Soc. Chem. Ind.*, 1919, 730A.]

T. H. P.

Lipoids of the Heart Muscle. P. A. LEVENE and S. KOMATSU (*J. Biol. Chem.*, 1919, **39**, 83—89).—The analysis of the so-called lecithin fraction obtained from heart muscle demonstrates that this fraction is a mixture of lecithin and kephalin. When reduced by means of hydrogen in the presence of colloidal palladium, a product was obtained having all the properties of the crude hydrolecithin obtained from egg-yolk (Levene and West, A., 1918, i, 288, 421). From this mixture, by fractionation, hydrolecithin and hydrokephalin were isolated.

The opinion expressed by Fränkel and Linnert (A., 1910, i, 295) that individual organs of the same animal contain specific phosphatides appears to lack support. There is rather an indication that the number of individual lipoids is limited, and that practically all animal organs contain the same lipoids. J. C. D.

Kephalin. VI. The Bearing of Cuorin on the Structure of Kephalin. P. A. LEVENE and S. KOMATSU (*J. Biol. Chem.*, 1919, **39**, 91—104).—The components of kephalin hitherto isolated are phosphoric acid, glycerol, aminoethyl alcohol, and stearic and linoleic acids. A molecule composed of equimolecular proportions of these would demand a different percentage composition from that usually found. The discrepancy could be explained on one of three grounds: first, that kephalin possesses a structure different from the one expressed by the above method; secondly, that kephalin isolated by the usual methods represented a substance modified in the course of preparation; and thirdly, that a substance of unknown composition was present as an impurity. The recent work of Levene and West (A., 1918, i, 421) on the preparation of a reduced kephalin possessing an elementary composition required by a molecule constituted as above excludes the first of the three alternatives. The work recorded in this paper shows that kephalin as usually prepared is a mixture of true kephalin with its own decomposition products. This explains the widely different

analytical data recorded by previous workers. One of the decomposition products is kephalin from which one fatty acid has been removed either by chemical manipulation or by enzymes. Substances were also obtained which consisted of products of deeper deterioration than the loss of one acid molecule. This conclusion was arrived at in the course of an investigation into the chemical nature of cuorin.

Support is given to the view of Maclean ("The Lipins," London, 1918, 52), who doubted that cuorin is an individual substance. The greater part of cuorin is made up of crude kephalin.

J. C. D.

Preparation of Monochloroacetic Acid. L. J. SIMON and G. CHAVANNE (U.S. Pat. 1304108; from *J. Soc. Chem. Ind.*, 1919, **38**, 553A).—Monochloroacetic acid is prepared by heating trichloroethylene with sulphuric acid containing a small amount of water.

G. F. M.

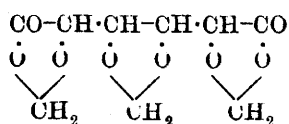
Oxidation of Lactic Acid by Bacteria with Formation of Pyruvic Acid and Ketonic Substances. P. MAZÉ (*Compt. rend. Soc. biol.*, 1918, **81**, 1150—1152; from *Chem. Zentr.*, 1919, i, 960).—The author has isolated a dozen types of bacteria which have the power of forming pyruvic acid and ketonic substances by the oxidation of lactic acid in a purely mineral nutrient solution and with calcium lactate as the sole source of carbon. The same types also produce pyruvic acid from similar solutions containing sugar, from which they form lactic acid; only in one instance does the alcoholic fermentation of sugar also occur. The course of the action has been more closely studied with six varieties, the pyruvic acid being estimated colorimetrically by Simon's reaction; for this purpose, the content of the solution must lie between 0.1 and 1%. Formation and decomposition of pyruvic acid occur at different rates with the various species. The yield of acetic acid varies from traces to more than 50% of the lactic acid decomposed, but formic acid is never produced. Two species produce, further, acetylmethylcarbinol and dimethyl diketone, whilst one species produces the latter only. The processes involved are indicated by the equations $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H} + \text{CH}_3\cdot\text{CO}\cdot\text{CO}_2\text{H} + \text{O} = \text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{C}(\text{OMe}) + 2\text{CO}_2 + \text{H}_2\text{O}$ and $2\text{CH}_3\cdot\text{CO}\cdot\text{CO}_2\text{H} + \text{O} = \text{CH}_3\cdot\text{CO}\cdot\text{CO}\cdot\text{CH}_3 + 2\text{CO}_2 + \text{H}_2\text{O}$. Dimethyl diketone might possibly be formed by direct oxidation of the secondary alcoholic group of acetylmethylcarbinol, but the complete absence of butylene glycol renders this improbable.

H. W.

Quantitative Studies on the Succinic Oxidone of Battelli and Stern. HANS EINBECK (*Biochem. Zeitsch.*, 1919, **95**, 296—305. Compare Battelli and Stern, *A.*, 1913, i, 929).—It appears probable that two quite distinct processes may take place when succinic acid is acted on by muscle pulp in the presence of oxygen. First, there is the elimination of two atoms of hydrogen with the formation of fumaric acid. This reaction is quantitative,

the amount of oxygen required being proportional to the amount of succinic acid in the reaction mixture. Then there is the addition of a molecule of water at the unsaturated linking of the fumaric acid, with the formation of *i*-malic acid. This reaction is not quantitative, but tends to an equilibrium, at which approximately a quarter of the fumaric acid remains unchanged. J. C. D.

Behaviour of the Methylene Group United to the Carboxyl Group in Trimethylenesaccharic Acid. CESARE PADARI (*Arch. farm. sper. sci. aff.*, 1918, **26**, 274—282; from *Chem. Zentr.*, 1919, iii, 65).—Opportunity is afforded by trimethylenesaccharic acid (annexed formula) of further investigation



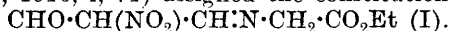
of the author's views on the relative stability of methyl groups which esterify hydroxy-groups or hydroxy- and carboxyl groups respectively (compare A., 1917, i, 716). The acid is hydrolysed by boiling water containing a small quantity of sulphuric acid to monomethylenesaccharic acid and formaldehyde. A similar fission appears to occur in the rabbit, since formaldehyde can be detected in the urine after administration of the acid. H. W.

Linoleic Acid and its Derivatives. KATSUMI TAKAHASHI (*J. Tokyo Chem. Soc.*, 1919, **40**, 233—289).—Linoleic acid can be estimated only by converting it into its derivatives. Physical and chemical properties, however, of both the bromo- and hydroxy-derivatives into which linoleic acid is ordinarily converted are confusing according to the different authors (compare Reformatzky, A., 1890, 362). Furthermore, the value obtained by the tetrabromostearic acid method is invariably less than that calculated from the iodine number in the presence of another unsaturated fatty acid. In order to investigate the source of this discrepancy, the author made extensive studies of the properties of various derivatives of linoleic acid. Linoleic acid is first separated by brominating linoleic acid from oil of rice bran and soja bean. This tetrabromostearic acid, which he designates as (A)-bromo-derivative, after repeated crystallisation from light petroleum, forms white, needle-shaped crystals, m. p. 114°. It is soluble in ether, but insoluble in light petroleum at the ordinary temperature. When converted into the methyl ester by Rollett's method, and hydrolysed to linoleic acid, a 90% yield calculated on the basis of the (A)-bromo-derivative, or 97% if calculated on the basis of its methyl ester, was obtained. An analysis shows its composition to be exactly that of linoleic acid. When this is again brominated, it yields three types of bromo-derivatives, regardless of the kinds of solvent used: (α) m. p. 113·5—114°, containing 53·38% of Br, insoluble in light petroleum; (β) m. p. 59—60°, containing 53·35% of Br, soluble in light petroleum; (γ) liquid, containing 52·86% of Br, soluble in light petroleum. Since the theoretical value for

tetrabromostearic acid, $C_{18}H_{32}O_2Br_4$, is 53·33% of Br, he concludes all these three varieties of bromo-derivatives must be tetrabromostearic acid. The yields of the three derivatives vary somewhat with the types of solvent used. With light petroleum as solvent, 43—46% of the total yield is in the α -form, the remaining 49·2% to 52·66% being β and γ ; with carbon tetrachloride, 39% α and 56% β and γ ; with ethyl ether, 47% α , 51·77% of β and γ ; with glacial acetic acid, 35% of α . In all cases, the α -form, which possesses exactly the same physical properties as the parent compound (that is, tetrabromostearic acid, m. p. 114° , soluble in light petroleum), is obtained only in a quantity of 49% of the (A)-bromo-derivative, the remaining portion being the same tetrabromostearic acid but having entirely different physical properties. When the α -variety is again reduced to linoleic acid and brominated for a third time, it gives 42·4—46% of the α -form and 52·8—55·8% of β and γ . From the β -form, 36·7% of the α , 48% of β , and 22·4% of γ ; from the γ -form, 24—26% of α , 8·05—8·4% of β , but 67·95—65·35% of γ are obtained. In general, all three racemic varieties of tetrabromostearic acid can be reduced to linoleic acid, and on further bromination each yields three varieties of bromo-derivatives, always, however, giving most of its own kind. The oxidation products of linoleic acid obtained from the α - and β -forms are a large quantity of sativic acid, m. p. 174° , and a small quantity of another tetrahydroxystearic acid, m. p. 135° . The linoleic acid obtained from the γ -form yields neither sativic acid nor the other tetrahydroxystearic acid, but gives an acid, $C_{16}H_{31}O_2\cdot OH$, soluble in water and a rosin-like substance insoluble in water and having the formula $(C_5H_8O_2)_n$. By applying the same method to the natural linoleic acid in the presence of unsaturated fatty acids, only 40% of the original amount of linoleic acid is obtained as the crystallised tetrabromostearic acid insoluble in light petroleum. The author proposes, therefore, a factor 2·5 to be used for linoleic acid estimations if it is to be isolated as the insoluble tetrabromostearic acid. Several analytical data are given to show that this factor is most satisfactory.

CHEMICAL ABSTRACTS.

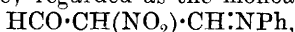
Condensation of Amino-compounds with Nitromalon-aldehyde. WILLIAM J. HALE and EDWARD M. HONAN (*J. Amer. Chem. Soc.*, 1919, **41**, 770—776).—To the aldehydic intermediate product formed in the preparation of carbopyrrolic esters by the condensation of aminoacetic esters with nitromalon-aldehyde, Hale and Hoyt (A., 1916, i, 71) assigned the constitution



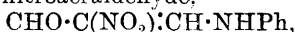
It is now found that such intermediate product is capable of formation in dilute alkaline solution, from which it separates readily. The substance separating is not, however, a salt, and is transformed by warm alkali into a pyrrole derivative, which the Hinsberg reaction and the Liebermann nitrosoamine reaction show to be a secondary amine. This intermediate compound must therefore have the constitution $CHO\cdot C(NO_2)\cdot CH\cdot NH\cdot CH_2\cdot CO_2Et$, the

isonitro-compound (I) first produced undergoing intramolecular rearrangement with transfer of the labile hydrogen atom from the central carbon to the nitrogen.

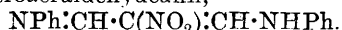
The assumption that the intermediate compound possessed the structure (I) was based on the results of Hill and Torrey (A., 1899, i, 788), who ascribed similar constitutions to a number of products resulting from the condensation of nitromalonaldehyde with amino-derivatives. With aniline, these authors obtained two compounds which they regarded as the monoanil,



and the dianil, $\text{NPh}\cdot\text{CH}\cdot\text{CH}(\text{NO}_2)\cdot\text{CH}\cdot\text{NPh}$; neither of these compounds exhibits any tendency to form salts, and as they are now found to be secondary amines, they must be regarded respectively as β -anilino- α -nitroacraldehyde,

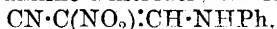


and β -anilino- α -nitroacraldehydeanil,



The similar compounds furnished by *p*-toluidine and by methylamine and its derivatives must receive analogous formulæ.

The action of 1 mol. of hydroxylamine on nitromalonaldehyde gives an unstable compound which immediately undergoes intramolecular condensation to a β -nitroisooxazole, whereas excess of hydroxylamine gives a dioxime stable in alkaline solution. The action of aniline hydrochloride on the sodium salt of this dioxime precipitates Hill and Hale's anil-oxime (A., 1903, i, 401), which is formed also by the interaction of hydroxylamine and the so-called monoanil (see above), and must therefore be a β -anilino- α -nitroacraldioxime, $\text{NOH}\cdot\text{CH}\cdot\text{C}(\text{NO}_2)\cdot\text{CH}\cdot\text{NHPh}$; dehydration of this oxime gives a β -anilino- α -nitroacrylonitrile,



which Hill and Hale termed a nitrile-anil.

These facts render necessary a modification of Hale and Hoyt's interpretation (*loc. cit.*) of the condensation of nitromalonaldehyde with glycine ester; no rearrangement in the pyrrole molecule is necessary for condensation after the intramolecular rearrangement of compound (I).

The condensation of nitromalonaldehyde with β -alanine ethyl ester proceeds easily in slightly alkaline solution or in presence of sodium acetate. β -(β -carbethoxyethylamino)- α -nitroacraldehyde being formed. Further intramolecular condensation sufficient to render possible the isolation of a pyrrole could not be effected, the only indication of the formation of a pyrrole derivative being the reddening of a pine splinter held in the vapour produced when the compound was heated with concentrated hydrochloric acid.

The results obtained lead to the conclusion that, in aliphatic imino-compounds presenting an aldehyde group in such position that its possible inter-reaction with a methylene group adjacent to the imino-group may lead to a pyrrole, this condensation is highly favoured when the methylene group is attached to a carbethoxyl or other negative component. If, however, the carbethoxyl group

is once removed from the particular methylene group by the interposition of another methylene group, the influence of the carbethoxyl group becomes so slight that neither the first nor the second methylene group exhibits any marked tendency to condense with the aldehyde group.

α -Nitro- β -(β -carbomethoxyethylamino)acraldehyde,
 $\text{CHO}\cdot\text{C}(\text{NO}_2)\cdot\text{CH}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et},$

forms colourless prisms, m. p. 79° , and gives various reactions for aldehydes and also Liebermann's nitrosoamine reaction.

α -Nitro- β -(β -carbomethoxyethylamino)acraldehyde,
 $\text{NO}_2\cdot\text{C}_5\text{H}_7\text{O}\cdot\text{CO}_2\text{Me},$

forms colourless leaflets, m. p. 66° , and gives the same reactions as the preceding compound. T. H. P.

Thiocyanoacetone and its Derivatives and Isomerides.

JOSEPH TCHERNIAC (T., 1919, 115, 1071—1090).

Photosynthesis of Formaldehyde and Sugar. P. R. KÖGEL (*Biochem. Zeitsch.*, 1919, 95, 313—316).—A theoretical consideration, in which changes of the keto-enol type are held to be of importance in the photosynthesis of formaldehyde and sugar.

J. C. D.

Degradation of Sugars by Enzymes. H. VON EULER and O. SVANBERG (*Zeitsch. physiol. Chem.*, 1919, 105, 187—239).—The course of the fermentation of sugars by a top yeast and a torula in an alkaline medium ($p_{\text{H}}=8$) has been studied. Under these conditions, alcohol and carbon dioxide are produced in equivalent amounts representing, for both products, 30—33% of the fermented sugar. Dextrose and lævulose, as well as invert-sugar, are rapidly fermented at $p_{\text{H}}=8$, but mannose and galactose are less readily attacked. Sucrose is fermented as rapidly as dextrose at this degree of alkalinity, but maltose remains untouched. These observations indicate that invertase is active at $p_{\text{H}}=8$, but that maltase is not. The inversion of sucrose was quantitatively studied as far as $p_{\text{H}}=8.5$ by repressing the fermentation by means of additions of toluene. The influence of a number of poisons on the fermentation in an alkaline medium is described. More or less marked inhibition was caused by chloroform, toluene, acetaldehyde, aniline, pyridine, resorcinol, sodium picrate, and phenol. Sodium salicylate caused a slightly increased rate of fermentation, whilst sodium lactate, chloroacetic acid, adrenaline, thyroid extract, and sodium thiosulphate had no appreciable effect. Drying at the ordinary temperature did not affect the activity of a yeast at $p_{\text{H}}=8$. The growth of yeasts in alkaline solutions has also been investigated. J. C. D.

Occurrence of Difficultly Reducing Carbohydrates in Urine. RAGNAR BERG (*Deut. Med. Woch.*, 1919, 45, 435—436; from *Chem. Zentr.*, 1919, iii, 33).—It has long been known that certain urines which do not contain dextrose have the

power of reducing copper sulphate; the solution becomes milky, and finally, particularly when preserved, a yellow, more or less heavy, flocculent precipitate separates which differs completely from the heavy, red precipitate produced by sugar. The author has been able to isolate the difficultly reducing sugar, which appears to be identical with Leo's sugar, in the form of colourless needles, about 2 mm. in length. It is found that urine (in the presence or absence of sugar), which gives the characteristic reaction after fermentation, also exhibits lævorotation. The reaction is frequently observed in cases of diabetes and neurasthenia, and particularly of gout. The author therefore designates the substance *arthritis*.
H. W.

Chitose. WALTHER ARMBRECHT (*Biochem. Zeitsch.*, 1919, **95**, 108—123).—Chitosan is completely dissolved by the action of nitrous acid. The solution contains carbohydrates of more than one type, but no crystalline sugar could be isolated. A crystalline osazone, m. p. 202° , was isolated from this mixture. This product is apparently identical with the osazone of chitose. From the products obtained by oxidising the crude "chitose syrup" with nitric acid, a monocarboxylic acid was obtained, which forms a cinchonine salt, colourless prisms, m. p. 200° , and may possibly contain a hydrofuran ring.
J. C. D.

Epifucose. E. VOTOČEK and J. ČERVENÝ (*Zeitsch. Zuckerind. Böhm.*, 1917, **42**, 215—217).—Fuconic acid is converted into epifuconic acid by treatment with pyridine and water, and the lactone of the latter acid is reduced by sodium amalgam to *epifucose*, which was isolated as a sweet, viscous, pale yellow syrup, and did not crystallise even after preservation during six months; it has $[\alpha]_D$ ca -9° . The phenylosazone, m. p. $177-178^{\circ}$ (decomp.), and the *p*-bromophenylosazone, m. p. 204° , are identical with the products obtained from fucose.
H. W.

Plant Colloids. VII. Diastase Action. M. SAMEC (*Koll. Chem. Beihefte*, 1919, **10**, 289—304. Compare A., 1914, i, 930; 1915, i, 941).—The processes occurring in the diastatic fermentation of starch have been investigated in the following manner: 10 grams of potato starch were heated with 900 c.c. of water at 120° for half an hour, then cooled to 50° and kept at this temperature, 100 c.c. of 1% diastase solution added, and the reaction allowed to proceed at 50° . At measured intervals of time, 25 c.c. of the reaction mixture were removed and heated rapidly to 100° to stop the action, and then cooled to 25° , at which temperature it was examined. The samples were measured to find, respectively, (i) the molecular weight of the non-dialysable fraction of the products of hydrolysis, that is, the portion with molecular weight greater than 2000—the freezing-point method was used for this purpose; (ii) the colour produced with iodine; (iii) the optical rotation; (iv) the reducing action on Fehling's solution; (v) the

specific conductivity; (vi) the hydrogen-ion concentration; (vii) the velocity of cataphoresis; and (viii) the content of phosphoric acid. The whole of these factors were plotted against the time during which the reaction had been proceeding, and from the curves produced, the following mechanism of the process is deduced. Under the influence of the ferment, the starch molecule decomposes into at least two unequal parts. Of these, one is very like starch in its properties; the other (dialysable) has a somewhat similar structure, since it colours iodine blue. The constitution of the starches and the dextrins appears to be almost analogous, since the optical rotation of both is very similar. The dialysable product possesses marked reducing properties. As the reaction proceeds, the colloidal starch residue separates products of high molecular weight which are more easily dialysable and give a blue iodine reaction. When the molecular weight of the colloidal residue has sunk to below 20,000, the dextrin molecules which separate give a red iodine reaction, and as the process continues they do not give an iodine reaction at all. The initial dextrin products are further decomposed, forming erythro-dextrins and sugar, and the erythro-dextrins pass over into achroo-dextrins. A tabulated scheme of the process, giving molecular weight and iodine reaction at the various stages of the process, is included in the paper.

J. F. S.

The Acetyl Content of Lignin. HANS PRINGSHEIM and HANS MAGNUS (*Zeitsch. physiol. Chem.*, 1919, **105**, 179—186).—The author has investigated the origin of the acetic acid produced in the dry distillation of wood and in the processes by which wood and straw are broken down by digestion with alkali. In the latter process, the whole of the acetic acid formed is derived from the lignin substance when the digestion is carried out without heating. If, however, the wood or straw is treated with a solution of sodium hydroxide at the b. p., with or without the use of increased pressure, a small fraction of the acetic acid formed has its origin in cellulose.

The lignin prepared according to the method of Willstätter and Zechmeister (*Zeitsch. angew. Chem.*, 1919, **32**, 41) is not identical with the natural product, since it has undergone hydrolysis and lost its acetyl groups. The natural product may be regenerated by acetylation. The lignin from hornbeam contains nearly double the number of acetyl groups found in lignin from pine-wood.

J. C. D.

Sulphite Liquors. KARL H. A. MELANDER (*Tekn. Tidskr.*, 1918, **10—12**, pp. 36; from *Chem. Zentr.*, 1919, i, 862—863).—By treatment of sulphite liquor with sodium chloride, the author has obtained a substance which differs considerably in its properties from that prepared by Klason by precipitation with calcium chloride; after purification, it forms a mixture of similar ligninsulphonic acids of high molecular weight in

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which a portion of the sulphur dioxide is loosely held in ester-like combination. The author designates the mixture *α-lignin-S-acid*, and has shown that the main portion of it is monobasic, whilst only a small part is dibasic. Vanillic acid, protocatechuic acid, and catechol are formed when it is fused with alkali under various conditions. Acetic acid and small amounts of higher fatty acids are also produced, thus pointing to the presence of acetyl groups. The yield of catechol attains 10% of the organic matter of the original substance. Free *α-lignin-S-acid* is obtained as a pale brown powder, which readily becomes resinified when hydrochloric acid is added to the solution of the salted-out product. It is hydrolysed by treatment with alkali. There appears to be little prospect of obtaining the acid in the crystalline condition, since analyses indicate that it is a mixture of relatively complex compounds of almost identical percentage composition. In the *salts* with naphthylamine and toluidine, an atom of nitrogen is present for each atom of sulphur; the latter, however, appears to be present in different forms, partly firmly and partly loosely combined, in the acid. The *sodium* salt is described. The brown colour of *α-lignin-S-acid* renders its titration in the presence of indicators a matter of difficulty. The equivalent, 782, is obtained by titration with sodium hydroxide and determination of the end-point by measurement of the electrolytic conductivity of the solution. Comparison of the potential of the solution against that of a calomel electrode gave the value 882 for another specimen. In certain cases, the use of phenolphthalein was also found possible, and the results show that the presence of an atom of sulphur in the free acid corresponds with that of one ionisable hydrogen atom, so that a carboxyl group cannot be present. The sodium salt is not perceptibly hydrolysed; determinations of the molecular weight in aqueous solution by the freezing-point method gave values between 822 and 991 for different specimens. The electrolytic conductivity of aqueous solutions of the sodium salt at different dilutions has also been determined.

H. W.

Preparation of Butylamine and of *n*-Dibutylamine. The Separation of Aliphatic Amines by Partial Neutralisation. EMIL ALPHONSE WERNER (T., 1919, 115, 1010—1014).

Biochemical Formation of Aminoethyl Alcohol from Serine. F. F. NORD (*Biochem. Zeitsch.*, 1919, 95, 281—285).—Aminoethyl alcohol was isolated from the products of the decomposition of serine by putrefactive bacteria. Ten grams of the amino-acid yielded 2·8 grams of crude aminoethyl alcohol picrolonate.

J. C. D.

The Muscarine Question. I. Double Salts of certain Bases with Platinum. ALBERT B. WEINHAGEN (*Zeitsch. physiol. Chem.*, 1919, 105, 249—257).—Choline platinibromide, $(C_6H_{14}ON)_2PtBr_6$,

large, dark red prisms or octahedra, m. p. 240° (decomp.), is sparingly soluble in cold water. Choline hydrobromide gives a

dark red precipitate with chloroplatinic acid. This double salt crystallises from water in prisms and plates, m. p. 255° (decomp.). It is apparently the compound $(C_5H_{14}ON)_2PtClBr_5$. Betaine platinibromide crystallises from water in dark red four- or six-sided prisms which decompose at 240° . Pyridine platinibromide, $(C_5H_5N)_2H_2PtBr_6$, dark red, short prisms, decomposes at about 280° . On heating the aqueous solution of this salt, a finely crystalline, golden-yellow double salt separates, $(C_5H_5N)_2PtBr_4$, which chars at about 150° . In the course of this change, an intermediate product, $[Pt(C_5H_5N)Br_5]HC_5H_5N$ (?), was isolated.

Arecaidine platinibromide, $(C_7H_{11}O_2N)_2H_2PtBr_6 \cdot H_2O$, forms dark red, eight-sided prisms, and also cinnabar-red, thin, rhombic plates, decomp. 238° . If a solution containing arecoline hydrobromide and chloroplatinic acid is warmed, it turns dark red, and a dark red double salt crystallising in six-sided plates and short prisms separates. This is apparently $(C_8H_{13}O_2N)_2H_2PtCl_2Br_4$.

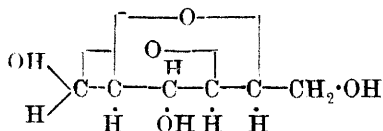
Nicotine platinibromide, $C_{10}H_{14}N_2 \cdot H_2PtBr_6 \cdot H_2O$, minute, dark red crystals, decomposes at 230° . It is decomposed by water with formation of an orange-yellow product.

No double salts were isolated and identified in the case of morphine and hydrazine.

J. C. D.

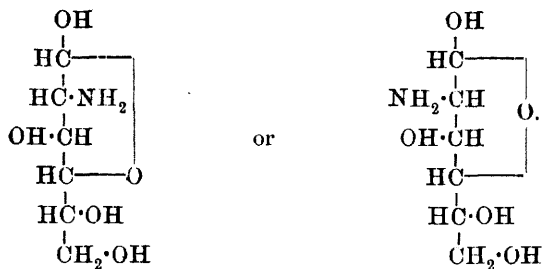
Epichitosamine and Epichitose. P. A. LEVENE (*J. Biol. Chem.*, 1919, **39**, 69—76).—The synthesis of epichitosamine is given. This sugar and chitosamine constitute the first pair of epimeric hexosamines. By reduction of the lactone hydrochloride with sodium amalgam, the crystalline epichitosamine, $C_6H_{13}O_5N$, was obtained (hydrochloride, $C_6H_{13}O_5N \cdot HCl$, m. p. 187° [corr.], $[\alpha]_D^{20} -4.7^{\circ}$). The osazone has m. p. 205° , and the rotation is in accord with that found for glucosazone. Efforts to obtain the monocarboxylic acid failed, but on oxidation of the hydrochloride with nitric acid, saccharic acid was formed. From the hydrochloride, by the action of mercuric oxide, the sugar epichitose, m. p. 240° (corr.) (decomp.), $[\alpha]_D^{25} -96^{\circ}$, was prepared in a crystalline condition. It reduces Fehling's solution.

Epichitosamine and epichitose show no mutarotation. If, in the former case, this is ascribed to the presence of the betaine structure assumed by Irvine and Hynd (T., 1912, **101**, 1136), it would be expected that it would react differently from the other amino-sugars with nitrous acid. No such difference could, however, be detected. Attempts to oxidise the sugar failed. Another peculiarity of the sugar lay in its behaviour towards mercuric oxide. Whilst other sugars under this treatment were transformed into the corresponding amino-acids, epiglucosamine formed epichitose. Epichitose may be represented graphically:



A further peculiarity of epichitosamine was found in its behaviour towards nitrous acid. In this case, saccharic acid was obtained, and no dehydration with ring formation followed deamination.

Epichitosamine appears to be an α -amino-sugar, and there are reasons for believing that it is represented by one of the following formulæ:



J. C. D.

***d*-Chondrosamino- and *d*-Chitosamino-heptonic Acids.**
P. A. LEVENE and I. MATSUO (*J. Biol. Chem.*, 1919, **39**, 105—118. Compare Levene, A., 1916, i, 203, 712).—The present communication contains specific directions leading to satisfactory yields of chondrosaminoheptonic acid, and simplified directions for the preparation of chitosaminoheptonic acid. By the action of hydrocyanic acid on hexosamines, a mixture of the two epimerides is obtained. The *d*-chondrosaminoheptonic acids had $[\alpha]_D^{25} - 3.5^\circ$. By fractional crystallisation, a lævorotatory *d*-chondrosaminoheptonic acid, elongated prisms, m. p. 139° (corr.) (decomp.), and a dextrorotatory *d*-chondrosaminoheptonic acid, were separated. The former showed an original rotation, $[\alpha]_D^{20} - 8.25^\circ$, and an equilibrium value of $[\alpha]_D^{25} - 13.00^\circ$. This form predominated in the original mixture. *d*-*d*-Chondrosaminoheptonic acid has an initial rotation $[\alpha]_D^{25} + 42.5^\circ$ and an equilibrium rotation $[\alpha]_D^{25} + 65.0^\circ$. The *d*-chitosaminoheptonic acids with original rotation $[\alpha]_D^{20} + 4.0^\circ$ and equilibrium rotation $[\alpha]_D^{20} - 1.0^\circ$ were separated into a dextrorotatory *d*-chitosaminoheptonic acid, heavy prisms, m. p. 192° (decomp.), initial rotation $[\alpha]_D^{25} + 6.5^\circ$ and equilibrium rotation $[\alpha]_D^{25} + 2.75^\circ$, and a lævorotatory *d*-chitosaminoheptonic acid, prismatic needles, m. p. 139° (corr.) (decomp.), initial rotation $[\alpha]_D^{25} - 7.5^\circ$ and equilibrium value $[\alpha]_D^{25} - 12.0^\circ$. In the original mixture, the dextro-form predominates.

The attempt to isolate the deaminised heptonic acids in a satisfactory condition failed.

After oxidation with nitric acid after deamination, insoluble calcium salts were obtained, which on analysis appeared to be the calcium salts of trihydroxyglutaric acids. The calcium salts obtained from the two acids showed different optical rotation; that from chondrosaminoheptonic acid had $[\alpha]_D^{25} + 5.0^\circ$ (initial) and $[\alpha]_D^{25} + 1.5^\circ$ (equilibrium), whilst that from chitosamino-

heptonic acid had $[\alpha]_D^{25} + 10.0^\circ$ (initial) and $[\alpha]_D^{25} + 17.0^\circ$ (equilibrium). Theoretically, both aminoheptonic acids should yield the same trihydroxyglutaric acid. J. C. D.

Constitution of Carbamides. IX. The Interaction of Nitrous Acid and Mono-substituted Ureas. The Preparation of Diazomethane, Diazoethane, Diazo-*n*-butane, and Diazoisopentane from the Respective Nitrosoureas. EMIL ALPHONSE WERNER (T., 1919, 115, 1093—1102).

Cyanogen Chloride. CH. MAUGUIN and L. J. SIMON (*Compt. rend.*, 1919, 169, 474—476).—There are only two cyanogen chlorides. One, a volatile liquid, has the following constants: m. p. -6.5° , b. p. $+12.5^\circ/760$ mm., D_0 1.222, mean coefficient of expansion ($0-45^\circ$) 0.0019. The other chloride is a solid polymeride, m. p. 145° . The volatile chloride is prepared by the action of chlorine or an acidified solution of sodium hypochlorite on aqueous solutions of hydrogen cyanide, or of equimolecular proportions of sodium cyanide and hydrogen chloride. It is conveniently obtained by the electrolysis of solutions containing equimolecular proportions of hydrogen cyanide and chloride, using a graphite anode in a closed porous pot provided with a delivery tube leading to a freezing bath for the collection of the cyanogen chloride. The porous pot stands in a metal vessel, serving as the cathode, and containing dilute hydrochloric acid. The yield varies from 75 to 80% of the theory. The optimum concentration of the solutions is about 2 gram-mols. per litre, and under these conditions no appreciable hydrolysis of cyanogen chloride by the aqueous hydrochloric acid occurs. The method of Sérullas, namely, the action of chlorine on mercuric cyanide, gives precisely the same product as that obtained by the other methods. G. F. M.

α -, β - and γ -Trinitrotoluenes. HUGH RYAN and W. M. O'RIORDAN (*Proc. Roy. Irish Acad.*, 1918, 34, 175—193).—The sensitive product to the presence of which accidents with α -trinitrotoluene are attributed is usually regarded as derived from α -trinitrotoluene itself, but the assumption that it is derived from the β - or γ -isomeride is equally probable, and would be the more likely if the latter compounds were chemically more reactive than the α -compound. The behaviour of the three isomerides towards alkalis, amines, hydrocarbons, and aldehydes under comparable conditions has therefore been investigated, and also that of *s*-trinitrobenzene towards alkalis.

The action of aqueous alkali on *s*-trinitrobenzene yields (1) tetranitroazoxybenzene (compare Lobry de Bruyn, A., 1895, i, 653), which exhibits reactions similar to those of Anschütz and Zimmermann's tetranitroazoxytoluene; (2) a small proportion of a compound, m. p. $200-220^\circ$, which is possibly hexanitrodiphenyl (m. p. 234°).

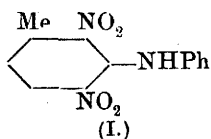
With sodium *n*-butoxide, α -trinitrotoluene gives a moderately stable compound, $C_6H_2Me(NO_2)_3 \cdot NaO \cdot C_4H_9$, which explodes when

dropped into a tube heated at 170° ; it is apparently accompanied by a small proportion of a di- or tri-alkyloxyde (compare Busch and Kögel, A., 1910, i, 472).

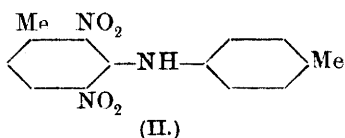
With either alkali hydroxide in presence of an oxidising agent (iodine) or hot alkali hydroxide or carbonate solution, α -trinitrotoluene gives hexanitrodibenzyl. When treated with alkali hydroxide or carbonate, β -trinitrotoluene yields a dinitro-*m*-cresol, m. p. 101° (compare Will, A., 1914, i, 509), and a large proportion of more complex products, whilst the γ -compound gives, in small amounts, a dinitro-*m*-cresol, m. p. $72-73^{\circ}$ (Will, *loc. cit.*), and a crystalline compound insoluble in alkali, possibly a dibenzyl or stilbene derivative. In all cases, dark, amorphous, explosive substances were isolated from the products of the action of alkalis.

α -Trinitrotoluene yields brown, complex compounds under the prolonged action of aqueous ammonia. With alcoholic ammonia, the β -compound reacts readily in the cold, giving β -dinitrotoluidine, m. p. $95-96^{\circ}$ (compare Hepp, A., 1883, 315); with aqueous ammonia, the β -compound yields a small proportion of β -dinitrotoluidine, and the γ -compound γ -dinitrotoluidine, m. p. $190-192^{\circ}$.

α -Trinitrotoluene forms an additive compound with *p*-toluidine (compare Jackson and Clarke, P., 1906, 83). With aniline, β -trinitrotoluene yields a phenyldinitrotolylamine, m. p. $114-115^{\circ}$, of the probable constitution (I) (compare Hepp, *loc. cit.*), and with *p*-toluidine, a dinitroditylamine, probably (II), which forms red, prismatic crystals, m. p. 131° . With

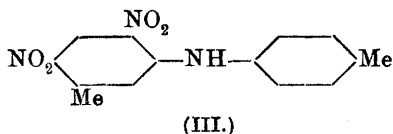


p-toluidine, γ -trinitrotoluene



gives an additive compound, $C_{14}H_{14}O_6N_4$, which crystallises in yellow needles, becomes orange-red at 147° , m. p. 154° ; in hot alcoholic solution, the reaction yields a dinitroditylamine, probably (III), which forms orange, monoclinic plates, m. p. 154° .

With aldehydes in presence of piperidine, α -trinitrotoluene condenses, giving (1) with benz-



aldehyde, 2 : 4 : 6-trinitrostilbene; (2) with anisaldehyde, 2 : 4 : 6-trinitro-4'-methoxystilbene (compare Pfeiffer and Monath, A., 1906, i, 413; 1916, i, 24); and (3) with

piperonaldehyde, 2 : 4 : 6-trinitro-3' : 4'-methylenedioxy-stilbene, $C_{15}H_8O_8N_3$, which crystallises from benzene in dull yellow prisms, turning scarlet on keeping or on being heated, owing to loss of benzene of crystallisation; m. p. (solvent-free), $156-157^{\circ}$. This reaction is not shown by either the β - or the γ -compound, even at 130° , only a brown, amorphous substance being obtained.

With phenanthrene, all three trinitrotoluenes form additive compounds, $C_{21}H_{15}O_6N_3$: (1) α -compound, bright yellow needles, m. p. 98—99°; (2) β -compound, pale yellow, prismatic plates, m. p. 105°; (3) γ -compound, dull yellow, acicular prisms, m. p. 83°.

The four substances examined react differently with alkalis, but in all cases reduction occurs, this probably proceeding to the formation of an amine, the amino-group of which is then replaced by hydroxyl with liberation of ammonia. Complex phenolic compounds are also apparently formed in considerable proportions. In the case of α -trinitrotoluene, this reduction is accompanied by an oxidation process, yielding hexanitrodibenzyl; non-phenolic compounds obtained from *s*-trinitrobenzene and γ -trinitrotoluene may also result from oxidation.

A sample of crude γ -trinitrotoluene was found to contain a dark, amorphous substance, which explodes when heated. T. H. P.

α - and β -Aminoalkyl(aryl)benzenes and their Derivatives.

A. OGATA (*J. Pharm. Soc. Japan*, 1919, **445**, 193—216).—For the study of the relation between the chemical constitution of amino-compounds and their local narcotic action, the author has prepared (1) five β -aminoalkyl(aryl)benzenes; (2) five α -aminoalkyl(aryl)benzenes; (3) four aryl derivatives of (1) and (2); (4) two *N*-alkylaryl derivatives of (1); and (5) three mixed secondary alkylamines. Primary amines can be prepared from nitriles by reduction with sodium. The author obtained β -phenylethylamine from phenylacetonitrile in 68% yield, and *isohexylamine* from *isohexonitrile*. β -Phenylisopropylamine, $CH_2Ph \cdot CHMe \cdot NH_2$, can easily be prepared by the action of ammonium formate (2 grams) on benzyl methyl ketone (2 grams) at 180—200°. Similarly were prepared β -aminoisohexylbenzene [β -amino- α -phenyl- δ -methylpentane], $CH_2Ph \cdot CH(NH_2) \cdot CH_2Pr^{\beta}$, b. p. 121°/8 mm. (hydrochloride, $C_{12}H_{19}N \cdot HCl$, m. p. 230—231°), β -amino-octylbenzene [β -amino- α -phenyloctane], $CH_2Ph \cdot CH(NH_2) \cdot [CH_2]_5 \cdot CH_3$, b. p. 145°/75 mm. (hydrochloride, m. p. 134—136°), $\alpha\beta$ -diphenylethylamine, α -phenylethylamine in 65% yield, α -aminoisohexylbenzene [α -amino- α -phenyl- δ -methylpentane], $NH_2 \cdot CHPh \cdot CH_2 \cdot CH_2Pr^{\beta}$, b. p. 146°/3 mm. (hydrochloride, m. p. 289°), and α -aminoheptylbenzene [α -amino- α -phenylheptane], $NH_2 \cdot CHPh \cdot [CH_2]_5 \cdot CH_3$, b. p. 145°/15 mm. (hydrochloride, m. p. 185—186°), from benzyl isobutyl ketone, benzyl *n*-hexyl ketone, deoxybenzoin, phenyl isoamyl ketone, and phenyl *n*-hexyl ketone respectively.

Secondary amines, such as di- β -phenylethylamine, benzyl- β -phenylisopropylamine, $CH_2Ph \cdot NH \cdot CHMe \cdot CH_2Ph$, b. p. 194°/24 mm. (hydrochloride, m. p. 186·5°), and benzyl- β -phenylethylamine have been obtained by reducing with sodium the condensation products of β -phenylethylamine and phenylacetaldehyde, of β -phenylisopropylamine and benzaldehyde, and of β -phenylethylamine and benzaldehyde respectively. *isoAmylisoheptylamine*, $CH_2Pr^{\beta} \cdot CH_2 \cdot NH \cdot CH_2 \cdot CH_2 \cdot CH_2Pr^{\beta}$, b. p. 208°/758 mm. (hydrochloride, m. p. 258—259°; stannichloride, m. p. 198°), was pre-

pared by the condensation of *iso*amyl bromide and *isohexylamine*, and *isoamylheptylamine*, $C_{12}H_{27}N$, b. p. $229^{\circ}/761$ mm. (*hydrochloride*, m. p. 235°), by the condensation of *iso*amyl bromide and *n*-heptylamine.

Tongue-tests proved that the hydrochlorides of β -amino- α -phenyloctane, $\alpha\beta$ -diphenylethylamine, α -phenylethylamine, benzyl- β -phenylisopropylamine, and *isoamylisohexylamine* have hypnotic action.

CHEMICAL ABSTRACTS.

Preparation of Explosives. THOMAS CAMPBELL JAMES, JAMES IVOR MORGAN JONES, and ROBERT ILLTYD LEWIS (Eng. Pat., 130357).—Trinitrophenylmethylnitroamine (tetryl) forms stable condensation products with aromatic amines, and these can be readily nitrated with warm nitric acid, forming nitro-compounds suitable for use as high explosives. In the case of trinitrophenylmethylnitroamine and aniline, picrylaniline, $C_6H_2(NO_2)_3 \cdot NH \cdot C_6H_5$, is obtained, and this, when nitrated, yields hexanitrodiphenylamine.

C. A. M.

Action of Bromine on some Derivatives of Diphenylamine.

HUGH RYAN and WILLIAM O'RIORDAN (*Proc. Roy. Irish Acad.*, 1919, **34**, 218—225).—The method given by Berger (compare Buisson, "*Le Problème des Poudres*") for the estimation of the total amount of diphenylamine, either free or as nitroso-derivative, present as stabiliser in a powder, depends on the conversion of the base into its tetrabromo-compound. By boiling the powder with dilute sodium hydroxide solution, the diphenylnitrosoamine is converted into diphenylamine; the distillate is then treated with excess of bromine, and the amount not used in the formation of the tetrabromodiphenylamine estimated volumetrically.

The authors' experiments show that the prolonged action of bromine on diphenylnitrosoamine in chloroform solution and in presence of sunlight yields mainly hexabromodiphenylamine, m. p. 223° (compare Gnehm, this Journal, 1876, 83), which is also obtained under similar conditions from tetrabromodiphenylamine; the latter represents the first product of the action of bromine on diphenylnitrosoamine.

Since some of the nitro-derivatives of diphenylamine and diphenylnitrosoamine are appreciably volatile in steam, and would hence accompany the diphenylamine in the distillate of Berger's method, the action of bromine on 4-nitro-, 2:10-, and 4:10-dinitrodiphenylnitrosoamines, 2:4-, 2:10-, and 4:10-dinitrodiphenylamines, and 2:4:8:10-tetranitrodiphenylamine has been investigated; of these compounds, the first three and the last have been found among the products of the interaction of diphenylamine with the oxy-acids of nitrogen. With the exception of the tetranitro-compound, all these compounds react with bromine in chloroform solution, the only product being in each case a dibromo-derivative. The derivatives of diphenylnitrosoamine lose the nitroso-group on bromination and yield the same bromo-compounds as the corresponding nitrodiphenylamines.

It is evident that Berger's method (see above), and also that of Dreger (A., 1909, ii, 708), will give untrustworthy results if any of the volatile nitro-compounds formed from diphenylamine in a powder escape interaction with the alkali, or if a mixture of tetra- and hexa-bromodiphenylamines is formed in consequence either of rise of temperature caused by rapid addition of the bromine or of prolonged contact of the bromine with the product.

Dibromo-4-nitrodiphenylamine, $C_{12}H_8O_2N_2Br_2$, forms bright yellow needles, softening at 212° , m. p. 216° . *Dibromo-2:4-dinitrodiphenylamine*, $C_{12}H_7O_4N_3Br_2$, prepared from 2:4-dinitrodiphenylamine, forms orange, rhombic prisms, m. p. 195.5° , and may be identical with the compound, m. p. 196° , obtained by Leymann (A., 1882, 1057). *Dibromo-2:10-dinitrodiphenylamine* forms felted, yellow needles, m. p. $185-186^\circ$. *Dibromo-4:10-dinitrodiphenylamine* forms pale yellow needles, m. p. 247° . T. H. P.

Action of Nitric Acid and Nitrous Acid on Diphenylamine.

I. HUGH RYAN and PHYLLIS RYAN (*Proc. Roy. Irish Acad.*, 1918 **34**, 194—204).—The experiments here described were all carried out at the ordinary temperature and at low concentrations. Under these conditions, prolonged interaction of equivalent amounts of diphenylamine and nitric acid in acetic acid solution forms only the nitrate of the base, whilst when a greater proportion of the acid is taken, one portion of the amine is converted into a brown, resinous solid and another portion into nitro-derivatives of diphenylamine, among which the 2:10-dinitro-, 4:10-dinitro-, and 2:4:8:10-tetranitro-derivatives have been identified; in only one experiment was a trace of 2:10-dinitrodiphenylnitrosoamine obtained.

Under similar conditions, the nitration of diphenylnitrosoamine proceeds quite differently. When two or more equivalents of nitric acid are used per one equivalent of diphenylnitrosoamine, the colour of the solution changes slowly from orange to orange-yellow or yellow, with separation of the sparingly soluble 2:10-dinitrodiphenylnitrosoamine. The latter is not formed when only one equivalent of acid is employed, the products then being 4-nitrodiphenylnitrosoamine, and probably a small amount of 2-nitrodiphenylnitrosoamine. When larger proportions of nitric acid are employed, the acetic acid solution is found to contain 2:4:8:10-tetranitrodiphenylamine and 4:10-dinitrodiphenylamine, together with other polynitro-compounds which have not been isolated pure. Three apparently different dinitrodiphenylamines have been prepared; all of these are pale yellow and melt with decomposition, binary mixtures melting several degrees lower than either of the constituents. The fact that these three compounds lose nitric oxide when heated may have a bearing on the heat tests for nitrocellulose powders stabilised by addition of diphenylamine.

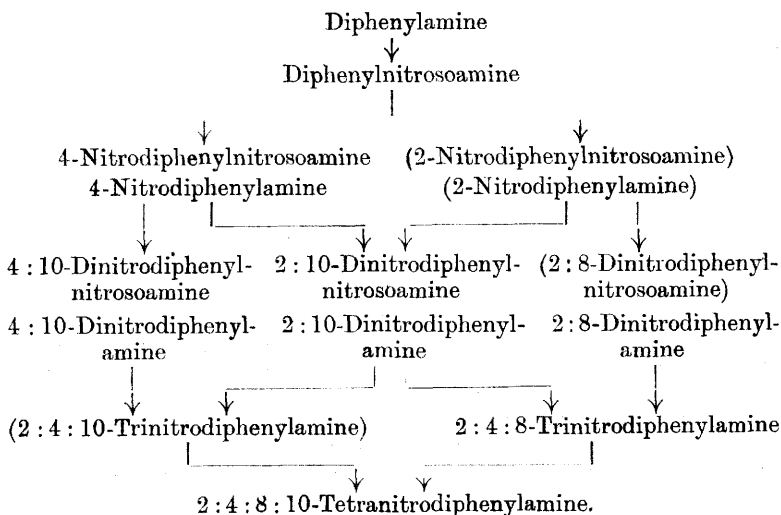
The action of nitric acid on diphenylamine in presence of nitrous acid has also been investigated. In this case, the main product is always a dinitrodiphenylnitrosoamine, the formation of which is

regarded as an indication of the completion of the stabilising action of the diphenylamine.

4:10-*Dinitrodiphenylnitrosoamine* (?), $C_{12}H_8O_5N_4$, obtained by the action in the cold of nitric acid of D 1.43 (6 mols.) on 4-nitrodiphenylnitrosoamine (1 mol.) in glacial acetic acid solution, is a yellowish-white solid, m. p. 155—159° (decomp.) T. H. P.

Action of Nitric Acid and Nitrous Acid on Diphenylamine.

II. HUGH RYAN and PHYLLIS RYAN (*Proc. Roy. Irish Acad.*, 1919, **34**, 212—217. Compare preceding abstract).—Owing to the ease with which the nitroso-group may be split off from nitrodiphenylnitrosoamines, the action of nitric acid on diphenylamine and diphenylnitrosoamine has been examined in the inert solvent, carbon tetrachloride. In this case, the reactions were complicated by separation of the solution into two layers with different relative concentrations of the reacting compounds, but in general the nitrations follow courses similar to those exhibited in acetic acid. Combination of the two sets of results gives the following scheme for the course of the reaction between nitric acid, nitrous acid, and diphenylamine at the ordinary temperature, and at low concentrations of the interacting compounds:



The compounds shown in brackets have not been isolated, but are probably present in some of the fractions obtained. T. H. P.

Melting Point of Pure Phenol. HENRI LEROUX (*J. Pharm. Chim.*, 1919, [vii], **20**, 88—91).—Pure phenol melts at 40.85° and boils at 182°/760 mm. Phenol is hygroscopic, and the presence of 0.2% of water lowers the melting point to 40°. W. P. S.

Process for the Preparation of Primary Alcohols.

SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE (Brit. Pat., 122630).—Ethylene oxide readily lends itself to the practical synthesis of primary alcohols provided that it is caused to react on an ethereal solution of an aromatic Grignard reagent in the gaseous form at temperatures between 0° and 10° instead of in ethereal solution at -15° , as hitherto employed. Under these conditions, almost theoretical yields are obtained. Examples are given of the synthesis of phenylethyl alcohol, *p*-tolylethyl alcohol, *p*-methoxyphenylethyl alcohol, and 6-methoxy-*m*-tolylethyl alcohol. [See, further, *J. Soc. Chem. Ind.*, 1919, October.] G. F. M.

Synthesis of certain Substituted Pyrogallol Ethers, including a New Acetophenetidine derived from the Ethyl Ether of Syringic Acid. MARSTON TAYLOR BOGERT and JACOB EHRLICH (*J. Amer. Chem. Soc.*, 1919, **41**, 798—810).—By conversion of the ethyl ether of syringic acid into the corresponding chloride and amide, and subjection of the latter to the Hofmann reaction, the authors have obtained 3:5-dimethoxyphenetidine, which on acetylation yields 3:5-dimethoxyacetophenetidine; this compound exhibits marked antipyretic properties, and is not more toxic than phenacetin. Syringic acid was obtained in 75% yield from 3:4:5-trimethoxybenzoic acid by a modification of Bogert and Isham's method (*A.*, 1914, **i**, 532).

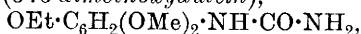
3:5-Dimethoxy-4-ethoxybenzoic acid (syringic acid ethyl ether), $\text{OEt} \cdot \text{C}_6\text{H}_3(\text{OMe})_2 \cdot \text{CO}_2\text{H}$, forms lustrous, white, sword-shaped needles, m. p. $123\text{--}124^{\circ}$ (corr.), and remains apparently unchanged at 300° . Its methyl ester, $\text{C}_{12}\text{H}_{16}\text{O}_5$, colourless, rhombic plates or long needles, m. p. $64\text{--}65^{\circ}$ (corr.), ethyl ester, hexagonal crystals, m. p. $46\text{--}47^{\circ}$ (corr.), b. p. $195\text{--}196^{\circ}/30\text{ mm.}$, and amide, $\text{C}_{10}\text{H}_{13}\text{O}_3 \cdot \text{CO} \cdot \text{NH}_2$, white, glistening leaves, m. p. $154\text{--}155^{\circ}$ (corr.), were prepared.

3:5-Dimethoxy-*p*-phenetidine (3:5-dimethoxy-4-ethoxyaniline), $\text{OEt} \cdot \text{C}_6\text{H}_3(\text{OMe})_2 \cdot \text{NH}_2$, forms pale brown needles, m. p. $92\text{--}93^{\circ}$ (corr.), and in the air undergoes gradual oxidation to a blue, amorphous substance. In aqueous solution, the amine gives a deep emerald coloration with ferric chloride and spangles of silver with silver nitrate. In concentrated sulphuric acid, it gives a colourless solution, but addition of the solid amine to concentrated nitric acid produces a deep crimson coloration, changing to clear yellow. When diazotised and coupled with α -(β -naphthol in alkaline solution, the amine yields a deep crimson (bright vermilion) dye.

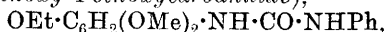
3:5-Dimethoxyaceto-*p*-phenetidine (3:5-dimethoxy-4-ethoxyacetanilide). $\text{OEt} \cdot \text{C}_6\text{H}_3(\text{OMe})_2 \cdot \text{NHAc}$, forms long, white needles, m. p. 129° (corr.), and also crystallises with $1\text{H}_2\text{O}$ in white prisms, m. p. 90° (corr.); it is not volatile in a current of steam. 2-Bromo-3:5-dimethoxy-4-ethoxyacetanilide, $\text{C}_{12}\text{H}_6\text{O}_4\text{NBr}$, was obtained crystalline.

3:5-Dimethoxy-4-ethoxyphenol, $\text{OEt} \cdot \text{C}_6\text{H}_3(\text{OMe})_2 \cdot \text{OH}$, to which the name *homoantiarol* (compare Kiliani, *A.*, 1897, **i**, 91; Graebe

and Suter, A., 1905, i, 703) is given, forms long, hair-like, pale yellow needles, m. p. 119° (corr.), and volatilises slowly even at 100° ; it responds to the ordinary reagents for free hydroxyl groups. 1-Iodo-3:5-dimethoxy-4-ethoxybenzene, $\text{OEt}\cdot\text{C}_6\text{H}_2\text{I}(\text{OMe})_2$, crystallises in yellow needles, m. p. 53° (corr.), and exhibits a powerful odour resembling that of iodoform. 3:5-Dimethoxy-4-ethoxyphenylcarbamide (3:5-dimethoxydulcin),



forms white needles, m. p. 182° (corr.), and, unlike dulcin, is practically tasteless. 3:5-Dimethoxy-4-ethoxy-s-diphenylcarbamide (3:5-dimethoxy-4-ethoxycarbanilide),



forms long, white, hair-like needles, m. p. 185° (corr.). 3:5-Dimethoxy-4-ethoxybenzeneazo- β -naphthol (3:5-dimethoxyphenetidineazo- β -naphthol), $\text{OEt}\cdot\text{C}_6\text{H}_2(\text{OMe})_2\cdot\text{N}:\text{N}\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$, forms dark red plates with a bronze-like lustre, m. p. 130° (corr.), and dyes silk and cotton salmon-pink and wool bright orange, the colours being fast against water, soap, dilute acid, and light. T. H. P.

Chemical Constituents of Bulbus Scillae. ERNST BUSCHMANN (*Arch. Pharm.*, 1919, 257, 79—86).—For purposes of investigation, it is essential to use fresh material, since the dried substance contains so much syrupy matter that the extraction of the active principles is practically impossible.

The coarsely powdered material was repeatedly extracted with cold water, and the extracts were treated successively with lead acetate, sodium phosphate, and ethyl acetate; the last removed a small quantity of yellow, crystalline material, the amount of which was too small for further investigation. The presence of choline in the residual aqueous solution was ascertained by the isolation of its platinichloride, m. p. 241° , and aurichloride, m. p. 261° . The residue left from the treatment with water was extracted with alcohol, and the extract was treated successively with light petroleum (b. p. not above 50°), ether, and chloroform. In this manner, there were obtained (i) xanthoscillide, lemon-yellow needles, m. p. 117 — 118° , which in an impure form constitutes Merck's scillin, scillisterol, m. p. 163 — 164° [acetate, m. p. 133 — 134° ; bromoacetate, m. p. 196° (decomp.)], phytosterol, m. p. 134° (acetate, m. p. 125 — 126°), and a brown oil (D 0.9248, iodine number 57.74—60.03, Köttstorfer number 192.65—199.22) in which the presence of formic and palmitic acids, probably also of acetic or propionic acid and oleic acid, was established; (ii) a phytosterol-glucoside, colourless, slender, indistinct needles, m. p. 290° (decomp.); and (iii) a small amount of long, slender needles which could not be further investigated.

The aqueous extract which had been treated with lead acetate gradually deposited a brownish-yellow precipitate, from which a strong organic acid was isolated, the investigation of which is not complete; a brown dye was also present. H. W.

Some Esters of *p*-Nitro- and *p*-Amino-benzoic Acid. S. V. HINTIKKA and LINDA MELANDER (*Ann. Acad. Sci. Fennicae*, 1919, [4], **10**, No. 13; from *Chem. Zentr.*, 1919, i, 836—837).—*Bornyl p-nitrobenzoate*, m. p. 134° , is prepared by heating a mixture of borneol and *p*-nitrobenzoyl chloride. *Camphenyl p-nitrobenzoate*, needles, m. p. 98° , is similarly obtained from camphenilol (m. p. $68-69^{\circ}$, $[\alpha]_D + 19.12^{\circ}$). *Fenchyl p-nitrobenzoate* crystallises in needles, m. p. $108-109^{\circ}$ (the fenchyl alcohol was prepared from fenchone and had $[\alpha]_D - 8.43^{\circ}$). *Bornyl p-aminobenzoate*, prepared by reducing the corresponding nitro-ester with stannous chloride and hydrochloric acid, forms needles or large, regular crystals, m. p. 144° , whilst its *acetyl* derivative crystallises in plates, m. p. 158° . Reduction of camphenyl *p*-nitrobenzoate leads to a mixture of the *amino*-ester, plates, m. p. 165° , and a substance, m. p. $126-129^{\circ}$. Attempts to reduce fenchyl *p*-nitrobenzoate by tin or stannous chloride and hydrochloric acid, or by zinc and acetic acid, led to resinous products. The action of hydrogen in the presence of colloidal palladium on an alcoholic solution of the fenchyl ester yielded a product, analyses of which gave results approximating to those required by the formula $C_{17}H_{23}O_2N$; it was an amino-compound, which, however, could not be purified. The ester could not be prepared from a mixture of *p*-aminobenzoic acid, fenchyl alcohol, and concentrated sulphuric acid, which yielded an oil, b. p. $166-168^{\circ}/10$ mm., D_4^{18} 0.9535, n_D^{18} 1.5193, the formation of which was due to the action of sulphuric acid on the alcohol; it is probably an unsaturated hydrocarbon of high molecular weight.

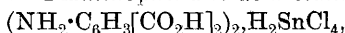
H. W.

Preparation of Organic Stanno- and Stanni-chlorides.
III. Compounds of the Amino-acids. J. G. F. DRUCE (*Chem. News*, 1919, **119**, 73—74. Compare *ibid.*, 1919, **118**, 1, 87).—The following organic derivatives of stannous and stannic chlorides have been prepared and characterised. *Anthranilic acid stannochloride*, $CO_2H \cdot C_6H_4 \cdot NH_2 \cdot H_2SnCl_3$, is prepared by warming 1.7 grams of *o*-nitrobenzoic acid with 3.6 grams of granulated tin and 30 c.c. of hydrochloric acid diluted with an equal volume of water. On cooling, after the solution of the tin, the salt separates in colourless, microcrystalline needles, which are washed with diluted hydrochloric acid and dried in the air. The salt softens at 85° and melts at 125° to a colourless liquid. A solution in hydrochloric acid gives a white precipitate with mercuric chloride and a brownish-black precipitate with hydrogen sulphide. This compound has also been prepared by crystallising the component salts together. *Anthranilic acid stannichloride*, $(NH_2 \cdot C_6H_4 \cdot CO_2H)_2 \cdot H_2SnCl_6$, is prepared by dissolving 3 grams of the first-mentioned compound in diluted hydrochloric acid and passing a slow stream of chlorine through the solution for three hours. On concentrating, deliquescent needles separate from the solution. This salt was also prepared by crystallising a mixture of the component salts. *m*-Aminobenzoic acid stannochloride, $(NH_2 \cdot C_6H_4 \cdot CO_2H)_2 \cdot H_2SnCl_4$, is prepared by an

analogous method to the first-named salt. It crystallises in a mass of feathery needles, m. p. 240° ; it is not very soluble in water, but the solution is strongly acid, and boiling does not cause hydrolysis. *m-Aminobenzoic acid stannichloride*, $(\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H})_2 \cdot \text{H}_2\text{SnCl}_6$, is prepared similarly to the corresponding ortho-compound. It forms short, radiating masses of colourless crystals, m. p. 193° . *p-Aminobenzoic acid stannichloride*, $(\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H})_2 \cdot \text{H}_2\text{SnCl}_6$, may be prepared by crystallising a mixture of the component salts or by reducing *p*-nitrobenzoic acid with tin and hydrochloric acid. Attempts to prepare the corresponding stannochloride yielded only the stannichloride. This compound crystallises in small, pale yellow, brittle needles, and does not melt at temperatures up to 315° . *Sulphanilic acid stannichloride*,



is prepared by crystallising a solution of the component salts from hot diluted hydrochloric acid. It forms a white, microcrystalline powder which is sparingly soluble in cold water. With warm water, metastannic acid separates; the salt does not melt, but darkens and decomposes at 270° . *4-Aminophthalic acid stannochloride*,



is prepared by reducing 4-nitrophthalic acid with tin and hydrochloric acid. It forms short, white needles, m. p. 274° ; it is soluble in cold water, but hydrolysed on heating. *4-Aminophthalic acid stannichloride*, $(\text{NH}_2 \cdot \text{C}_6\text{H}_3[\text{CO}_2\text{H}]_2)_2 \cdot \text{H}_2\text{SnCl}_6$, is obtained by warming 2 grams of 4-nitrophthalic acid and 6.9 grams of stannous chloride with 100 c.c. of diluted hydrochloric acid for two hours. It forms small, pale yellow crystals, m. p. 182° . *Aminosalicyclic acid stannichloride*, $(\text{NH}_2 \cdot \text{C}_6\text{H}_3[\text{OH}] \cdot \text{CO}_2\text{H})_2 \cdot \text{H}_2\text{SnCl}_6$, is prepared by reducing nitrosalicyclic acid with stannous chloride in alcoholic hydrochloric acid; it forms small, brown, prismatic crystals, m. p. 128° . It is soluble in water, but is hydrolysed on warming.

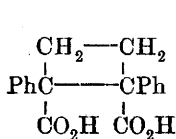
J. F. S.

Heterocinnamic Acids of Erlenmeyer, jun. A. W. K. DE JONG (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 1048—1054).—The author has repeated the experiments of Erlenmeyer by which the heterocinnamic acids were stated to be formed, and is unable to obtain these substances. It would therefore appear that these compounds are not pure substances and cannot be obtained from pure cinnamic acid.

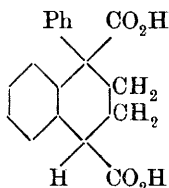
J. F. S.

Constitution of the *iso*Atropic Acids. L. SMITH (*Lunds Univ. Årsskr.*, 1919, [ii], **14**, 3—16; from *Chem. Zentr.*, 1919, i, 834—836).—Anhydrous atrolactic acid is smoothly transformed into α -isoatropic acid when heated at 140 — 160° in an atmosphere of carbon dioxide; at 200° , a mixture of the α - and β -acids, containing about 33% of the latter, is formed. Concentrated alkalis convert the α -acid into the β -acid. It is therefore possible that the

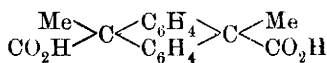
acids are *cis-trans*-isomerides, which is consistent with the formulæ previously proposed for them :



(I.)



(II.)



(III.)

The choice between these formulæ is rendered possible by the fact that the first contains two similarly situated asymmetric carbon atoms; the second has two dissimilar atoms, whilst the third does not possess an asymmetric carbon atom. Since α - and β -isoatropic acids can be resolved by phenylethylamine, formulæ I and III are excluded. If the acids are really *cis-trans*-isomerides, it should be possible to obtain the active *trans*-form from the active *cis*-form, and this can actually be effected by the action of sodium ethoxide on the *d*- α -acid, whereby the *d*- β -acid is produced. The action of alcoholic hydrogen chloride on the α -acid leads to the formation of a hydrogen ester which, when hydrolysed, yields a mixture of α - and β -isoatropic acids. The conversion, however, does not occur during esterification, as Liebermann assumed, but during hydrolysis. The hydrogen ester of the α -acid is an α -compound which, when hydrolysed in the cold, yields α -acid mixed with only 10% of the β -isomeride. The hydrogen ester of the β -acid belongs to the β -series, and, contrary to Liebermann's data, cannot be converted by heat or by crystallisation from acetic acid into the α -isomeride. β -isoAtropic acid and its hydrogen ester yield only β -acid and decomposition products when treated with acetic acid and concentrated hydrochloric acid. Attempts to effect the interconversion by means of ultra-violet light were unsuccessful.

α -isoAtropic acid, m. p. 238.5—239° (corr.), or rather lower when heating is effected too slowly, is best prepared by heating anhydrous atrolactic acid in an atmosphere of carbon dioxide during thirty hours at 140—160°. It is converted by boiling alcoholic sodium ethoxide or aqueous barium hydroxide solution into β -isoatropic acid, m. p. 208.5—209° (corr.). The latter can be resolved into its components with the aid of *l*-phenylethylamine in aqueous-alcoholic solution, when the salt of the *d*-acid separates. *d*- β -isoAtropic acid has m. p. 196.5—197.5° (corr.), $[\alpha]_D + 8.95^\circ$ in alcoholic solution. *l*- β -isoAtropic acid, m. p. 196.5—197°, $[\alpha]_D - 8.8^\circ$ in alcohol, is similarly obtained by the help of *d*-phenylethylamine. *d*- α -isoAtropic acid, prepared by resolving the *r*-acid with *d*-phenylethylamine, has $[\alpha]_D + 7.25^\circ$ in alcoholic solution, m. p. 239° after darkening, and softening at 234° when not too slowly heated. *l*- α -isoAtropic acid is isolated from the residues left

from the separation of the *d*-isomeride or by treatment of the laevorotatory mixture of acids which is then produced with *l*-phenylethylamine; it has $[\alpha]_D -7.26^\circ$ in ethyl-alcoholic solution. *Ethyl hydrogen β -isoatropate* crystallises in plates, m. p. 116° (corr.). *Ethyl hydrogen α -isoatropate* has m. p. 186° . H. W.

Camphenecamphoric Acid. S. V. HINTIKKA (*Ann. Acad. Sci. Fennicae*, 1919, [A], 6, iii; from *Chem. Zentr.*, 1919, i, 839—840).

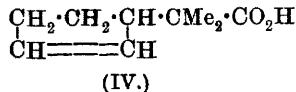
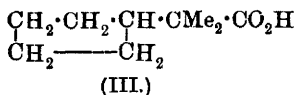
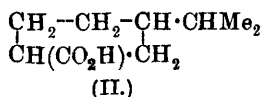
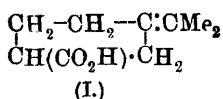
—It has been shown previously (A., 1914, i, 409) that carbocamphenilone is formed by the dry distillation of lead hydroxycamphenilane, and is converted by hydrogen peroxide into

camphenecamphoric acid, $\begin{array}{c} \text{CH}_2-\text{CH}_2-\text{CH}\cdot\text{CMe}_2\cdot\text{CO}_2\text{H} \\ | \\ \text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2 \end{array}$ (A., 1914,

i, 973). Doubt has been cast on the validity of this formula by Aschan (A., 1914, i, 692), but it may be regarded as established by Lipp's synthesis of the acid (A., 1914, i, 542) and by the complete synthesis of camphenilone (A., 1914, i, 852). The results of further investigations are most readily explained with the help of Lipp's formula. The constitution of carbocamphenilone (annexed

$\begin{array}{c} \text{CH}_2-\text{CH}-\text{CMe}_2 \\ | \quad | \\ \text{CH}_2 \quad \text{CO} \\ | \\ \text{CH}_2-\text{CH}-\text{CO} \end{array}$ formula) follows from its reconversion by sodium hydroxide into hydroxycamphenilanic acid. When camphenecamphoric acid is distilled under ordinary pressure (Aschan, A., 1911, i, 797), it yields a liquid, unsaturated acid, $\text{C}_9\text{H}_{14}\text{O}_2$, and an acid, $\text{C}_{10}\text{H}_{14}\text{O}_3$, m. p.

134° ; the former probably has the structure (I), since, when reduced with hydrogen in the presence of palladium, it gives an acid, $\text{C}_9\text{H}_{16}\text{O}_2$, which appears to be identical with dihydrocamphoceanic acid (II) (Bouveault and Blanc, A., 1908, i, 134; 1909, i, 108; Hintikka, A., 1914, i, 838).



For purposes of comparison, *cyclopentaneisobutyric acid* (III) has been prepared, since the formation of the corresponding unsaturated acid (IV) by the decomposition of camphenecamphoric acid is a possibility. The ketonic nature of the acid, $\text{C}_{10}\text{H}_{14}\text{O}_3$, is confirmed by the isolation of a phenylhydrazone; since the acid is converted by cautious heating with potassium hydroxide solution or by boiling with alcoholic sodium methoxide or ethoxide into camphenecamphoric acid, it may be regarded as camphenilone- α -carboxylic

acid (annexed formula). It is probably identical with the acid obtained by Houben and Willfroth (A., 1913, i, 970). The dry distillation of a number of salts of camphenecamphoric acid has been further investigated. The lead salt yields camphenilone, which is also obtained to some extent from the uranyl and ferric salts, but not from the calcium or copper salt.

The following data are recorded. Hydroxycamphenilanic acid has m. p. 176—177°, is optically inactive, and gives camphenilone with lead peroxide and sulphuric acid. The acid, $C_9H_{16}O_2$, prepared by reduction of the acid, $C_9H_{14}O_2$, has b. p. 138—139°/10 mm., and is stable towards permanganate; the corresponding *amide* forms leaflets, m. p. 169°. *cyclopentaneisobutyric acid* is a readily volatile oil prepared by the catalytic reduction and subsequent hydrolysis of ethyl *cyclopentaneisobutyrate*; the corresponding *amide* has m. p. 141—142°, whilst *cyclopentaneisobutyramide* melts at 136—137°. The *phenylhydrazone* of camphenilone- α -carboxylic acid, $C_{16}H_{20}O_2N_2$, has m. p. 142—143°. H. W.

Oxidation of Benzaldoxime. J. BOUGAULT and P. ROBIN (*Compt. rend.*, 1919, **169**, 341—343).—The oximes of the aldehydes which would apparently be formed by the elimination of carbon dioxide from α -ketonic acids during oxidation with iodine and sodium carbonate do not give on similar treatment the same products of oxidation as the oximes of the α -ketonic acids themselves. Thus, whilst the oxime of phenylglyoxylic acid gives benzonitrile and diphenylglyoxime peroxide, neither of these substances could be detected among the oxidation products of benzaldoxime. The oxime was treated in benzene solution with aqueous sodium carbonate and iodine. A precipitate of benzaldoxime peroxide, $CHPh:N \cdot O \cdot O \cdot N:CHPh$, was formed, and from the benzene layer benzoylbenzaldoxime, $CHPh:N \cdot OBz$, and dibenzenyloxoazoxime, $CPh \begin{smallmatrix} \diagup NO \diagdown \\ \diagdown NO \diagup \end{smallmatrix} CPh$, were isolated and identified. The latter two substances were separated by forming the easily decomposed iodine additive product of dibenzenyloxoazoxime, which is almost insoluble in ether. G. F. M.

Pungency of Synthetic Aromatic Ketones Related to Zingerone. LEONORE KLETZ PEARSON (*Pharm. J.*, 1919, **103**, 78—80).—The substances are of the type $CHPh:CH \cdot CO \cdot R$ and $CH_2Ph:CH_2 \cdot CO \cdot R$, where one or more hydrogen atoms of the benzene nucleus is replaced by one or more hydroxy- or methoxy-groups, and where R represents the methyl, ethyl, or phenyl radicle. Similar compounds have been studied from the same point of view by Nomura and Nozawa (A., 1918, i, 438); the authors have, however, been able to make several additional generalisations.

The primary, unsaturated condensation products alone, with the exception of *o*-hydroxystyryl methyl ketone, develop no appreciable

pungency on long contact with the tongue; in alcoholic solution, the pungency appears, as a rule, slowly. In the case of the corresponding saturated compounds, the pungency develops quickly, both alone and in alcoholic solution. β -3:4-Methylenedioxyphenylethyl methyl ketone is an exception in that it develops no appreciable pungency by itself. In every case, the unsaturated ketone was much more pungent than the corresponding saturated compound. The replacement of the hydrogen of the phenolic hydroxy-group of zingerone by an acyl radicle appears to have very little effect on the pungency of the compound. On the other hand, 3:4-methylenedioxystryryl methyl ketone and 3:4-methylenedioxyphenylethyl methyl ketone, though containing no free hydroxy-groups, are much more pungent than the corresponding 4-hydroxy-3-methoxy-derivatives, to which they are closely related.

The replacement of the *meta*-hydrogen of the benzene nucleus in *p*-hydroxyphenylethyl methyl ketone by a methoxy-group brings about a decided increase in pungency. The substitution of a bromine atom in this position appears to have a similar effect.

An increase in the weight of the side-chain causes a decided increase in the pungency of the compound. The exceptional pungency of *o*-hydroxystyryl methyl ketone is an outstanding feature of the experiments.

The experimental method of testing the substances consisted in dissolving the compound (0.1 gram) in alcohol (10 c.c.), diluting 1 c.c. of this solution to 3 c.c. or 10 c.c. with water or alcohol (or a mixture), and continuing the dilution in this way until the pungency was found to have become imperceptible. In the case of the more concentrated alcoholic solutions, one or two drops were placed on the tongue; the effect of the alcohol rapidly disappeared, and the pungency became perceptible. With more dilute aqueous solutions, a quantity was taken into the mouth and allowed to remain there for about three seconds.

4-Hydroxy-3-methoxystyryl ethyl ketone, prepared from vanillin and methyl ethyl ketone, is an almost colourless, crystalline solid, m. p. 94°. *3:4-Dihydroxystyryl methyl ketone* forms pale brown cubes, m. p. 176°. H. W.

Halogenation of Juglone : New Type of Naphthalene Dyes.

A. S. WHEELER and J. W. SCOTT (*J. Amer. Chem. Soc.*, 1919, **41**, 833—841).—Treatment of juglone (5-hydroxy-1:4-naphthaquinone) in acetic acid solution in the cold with chlorine or bromine yields juglone dichloride or dibromide, which loses one molecule of hydrogen haloid under the action of alcohol, giving 2-chloro-(or bromo-)juglone [2-chloro-(or bromo)-5-hydroxy-1:4-naphthaquinone]. In hot acetic acid solution, the action of chlorine on juglone forms 2:3-dichloro-5-hydroxy-1:4-naphthaquinone, whereas that of bromine under similar conditions yields 2:3:8-tribromo-5-hydroxy-1:4-naphthaquinone; both these compounds form acetyl derivatives, and treatment of the tribromo-derivative with alcoholic hydrochloric acid gives 8-chloro-2:3-dibromo-1:4-naphthaquinone.

Further, the 8-bromine atom of the tribromo-compound is replaced by hydroxyl by the action of alcoholic sodium hydroxide, 2:3-dibromo-5:8-dihydroxy-1:4-naphthaquinone resulting.

The tribromojuglone is a brilliant red compound, and constitutes a naphthalene dye of a new type. Its sodium salt, readily prepared by shaking its ethereal solution with aqueous sodium carbonate, is an indigo-blue compound, and dyes silk a fine champagne colour and wool a tan colour, which may be modified by the use of mordants; in both cases, the colour is fast against washing and ironing, and fades only after long exposure to a southern light. Cotton requires a mordant, and, when tannin is used in this capacity, assumes an écreu colour. According to its constitution, juglone itself should act as a dye, but attempts to prepare its sodium salt result in its oxidation, whilst careful halogenation of juglone in the cold yields an unstable additive product.

5-Hydroxy-1:4-naphthaquinone 2:3-dichloride (juglone dichloride), $C_{10}H_6O_3Cl_2$, forms lemon-yellow plates, turning brown at 150° , m. p. $159-160^\circ$.

2-Chloro-5-hydroxy-1:4-naphthaquinone (2-chlorojuglone),
 $C_{10}H_5O_3Cl$,

forms small, flat, yellowish-brown needles, and emits violet vapour at above 130° , m. p. 166° . Its *acetyl* derivative, $C_{12}H_4O_4Cl$, crystallises in transparent, brownish-yellow plates, m. p. 147° .

2:3-Dichloro-5-hydroxy-1:4-naphthaquinone (2:3-dichlorojuglone), $C_{10}H_4O_3Cl_2$, forms lustrous, golden-brown needles, m. p. 149° (dark red liquid); its *acetyl* derivative, $C_{10}H_3O_3Cl_2 \cdot OAc$, forms yellow plates, m. p. 154° (dark brown liquid).

5-Hydroxy-1:4-naphthaquinone 2:3-dibromide (juglone dibromide), $C_{10}H_6O_3Br_2$, forms rosettes and fan-shaped groups of yellow, pointed prisms, m. p. 109° .

2-Bromo-5-hydroxy-1:4-naphthaquinone (2-bromojuglone),
 $C_{10}H_5O_3Br$,

forms clusters of translucent, yellowish-brown plates, m. p. 166° (almost black liquid). Its *acetyl* derivative, $C_{10}H_4O_3Br \cdot OAc$, forms golden-brown plates, m. p. 148° (dark yellow liquid).

2:3:8-Tribromo-5-hydroxy-1:4-naphthaquinone (2:3:8-tribromojuglone), $C_{10}H_2O_3Br_3$, forms brilliant, deep red needles, m. p. 170° , and dissolves in concentrated nitric or sulphuric acid with a red coloration, and in hot sodium carbonate solution, yielding a purple liquid quickly changing to red. Its *sodium* derivative,

$C_{10}H_2O_3Br_3Na$,

dissolves readily in water or alcohol, and its *acetyl* derivative, $C_{10}H_2O_2Br_3 \cdot OAc$, crystallises in silky, yellow needles, m. p. 186° . Attempts to methylate tribromojuglone were unsuccessful, and oxidation by means of nitric acid or alkaline permanganate solution gave no definite product.

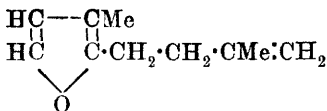
8-Chloro-2:3-dibromo-5-hydroxy-1:4-naphthaquinone (8-chloro-2:3-dibromojuglone), $C_{10}H_3O_3ClBr_2$, forms golden-bronze plates, m. p. 152° (dark red liquid).

2:3-Dibromo-5:8-dihydroxy-1:4-naphthaquinone (2:3-dibromo-

8-hydroxyjuglone), $C_{10}H_4O_4Br_2$, forms small, golden-brown, prismatic needles, and emits vapour at about 160° , m. p. 236° (black liquid). T. H. P.

Solubility of Camphor in Water. H. LEO and E. RIMBACH (*Biochem. Zeitsch.*, 1919, **95**, 306—312).—The solubility of camphor in water at the ordinary temperature is 1 in 598. In Ringer's solution under the same conditions, it is 1 in 577. The solubility falls with rise in temperature. The dissolution of camphor in water is an exothermic process. J. C. D.

Essential Oil of Perilla citriodora, Makino. HEISABURO KONDO and SEITARO YAMAGUCHI (*J. Pharm. Soc. Japan*, 1919, **446**, 263—275).—*Perilla citriodora*, Makino, which belongs to the *Labiatae* group, is known to contain an essential oil in an amount 2—3% of the weight of the dry leaf, having D 0.911 — 0.913 ; 59.26% of the oil is citral. The authors have investigated the chemical nature of the remaining portion of the oil after the citral is removed. This oil, after being dried over calcium chloride, can be distilled into five fractions under 25 mm. pressure: (1) 90 — 100° , 49%; (2) 100 — 120° , 5%; (3) 120 — 130° , 9%; (4) above 130° , 6%; (5) residue, 31%. From the first fraction they have isolated a substance which they have named *perillen*, b. p. 185 — 186° , $D^{20} 0.9017$, $n_D^{21} 1.47053$, $[\alpha]_D$ zero. Analysis gives the empirical formula $C_{10}H_{14}O$. There are only a few substances known to occur in plants having a similar composition, the best known being carvone and myrrol. *Perillen* differs from the former in b. p. and odour, and from the latter by the fact that the purple colour with bromine quickly changes to green. It contains one furan nucleus, one methyl group, and one side-chain with one double bond, which on oxidation yields $CH_2Pr^2 \cdot CH_2 \cdot CO_2H$. The annexed formula is suggested for this new oil. *Dihydroperillen* is obtained by reducing *perillen*, b. p. 182° , $D^{22} 0.8852$, $n_D^{22} 1.45762$. From the remaining fractions there was obtained a compound, b. p. 251° , $D^{11} 0.9088$, $n_D^{11} 1.50176$, $[\alpha]_D -4.358^\circ$, which is concluded to be a sesquiterpene.



CHEMICAL ABSTRACTS.

Uzarin from Gomphocarpus Root. LUDWIG KOFLER (*Arch. Pharm.*, 1917, **255**, 550—552).—Uzarin (compare Hennig, A., 1918, i, 94) may be readily obtained by extracting the root known as *Gomphocarpus spec.*, or Wasicky's ithongua (*Ber. deut. Pharm. Ges.*, 1916, **26**, 267), with methyl alcohol on the water-bath, evaporating the alcohol, treating the residue with boiling water, filtering the hot solution, and recrystallising the uzarin which separates on cooling, first from a mixture of methyl alcohol and ether, and afterwards from boiling water. The percentages of uzarin obtained in this way from the two products were 4.84 and 3.70 respectively. Uzarin has a slightly bitter taste, and is pre-

precipitated from aqueous solution by tannic acid, excess of which redissolves the precipitate. Various colour reactions of the glucoside are described. It begins to decompose at 190° . T. H. P.

Meconic Acid and its Behaviour in the Estimation of Morphine in Opium. A. HEIDUSCHKA and M. FAUL (*Arch. Pharm.*, 1917, **255**, 482—496).—Ammonium meconate separates in crystals containing $1\text{H}_2\text{O}$ when prepared in aqueous solution or in the anhydrous form, $(\text{NH}_4)_2\text{C}_7\text{H}_2\text{O}_7$, when prepared from meconic acid and ammonium acetate in absolute alcoholic solution; the salts are neutral towards iodeosin and dimethylaminoazobenzene. Calcium meconate has the formula $\text{C}_7\text{H}_2\text{O}_7\text{Ca}$, or, when dried at 110° , $\text{C}_{14}\text{H}_2\text{O}_{13}\text{Ca}_2$, both salts being neutral towards the above indicators; the solubility of the former in *N*/10-ammonia solution was measured at 18° .

The meconic acid contained in opium does not affect the results obtained in estimating the morphine by precipitation with ammonia (compare this vol., ii, 437). T. H. P.

Physiologically Active Constituents of Certain Philippine Medicinal Plants. III. A. H. WELLS (*Philippine J. Sci.*, 1919, **14**, 1—7).—The dry wood of *Arcangelisia flava* (Linn.) contains 4.8% of berberine, probably a higher percentage than that in any other Philippine plant. As the wood is soft and porous and contains but little extractive matter, the recovery of the alkaloid is simple, involving merely maceration with 95% alcohol, evaporation of most of the alcohol, and the recrystallisation of the salt formed by the addition of a mineral acid to the concentrated liquor. The plant is therefore an excellent source of the drug. *Cassia siamea* (Lam.) occurs only in cultivation as a shade tree. The pods, leaves, and branches contain a poisonous *alkaloid* having the empirical formula $\text{C}_{14}\text{H}_{19}\text{O}_3\text{N}$. The rhizomes of *Geodorum nutans* contain about 14% of a water-soluble adhesive gum of exceptional strength and lasting power. *Coriaria intermedia*, known in New Zealand as "toot plant," contains small quantities of a poisonous glucoside in its leaves and fruit. G. F. M.

Syntheses in the Cinchona Series. I. The Simpler Cinchona Alkaloids and their Dihydro-derivatives. MICHAEL HEIDELBERGER and WALTER A. JACOBS (*J. Amer. Chem. Soc.*, 1919, **41**, 817—833).—The reduction products of various cinchona alkaloids and certain synthetic homologues of these products are described. The reduction of cinchonine, cinchonidine, quinine, and quinidine to hydrocinchonine, hydrocinchonidine, hydroquinine, and hydroquinidine was readily effected by means of palladous chloride in dilute sulphuric acid solution (D.R.-P. 252136). The properties of the hydrogenated alkaloids obtained agree with those recorded for the natural compounds. Hydrocupreine may be prepared in large quantity by de-etherifying hydroquinine by means of boiling aqueous hydrobromic acid.

Hydrocupreine and its ethyl ether, which, as derivatives of hydro-

quinine, are lævorotatory, are compared with the corresponding dextrorotatory stereoisomerides derived from hydroquinidine. These, which are named hydrocupreidine and ethylhydrocupreidine, have not been previously described, although the former was evidently obtained crystalline by Forst and Böhringer (A., 1882, 1306) by heating hydroquinidine with hydrochloric acid in a sealed tube. Hydrocupreidine is readily isolated from hydroquinidine by the method used for preparing its lævorotatory isomeride, hydrocupreine, and it is easily converted into its ethyl ether by means of ethyl sulphate and alcoholic alkali.

Quinicine was prepared by isomerisation of quinidine in accordance with Miller, Rohde, and Fussenegger's instructions (A., 1901, i, 95), and was readily isolated in good yield as the monohydrochloride, which was unobtainable by other workers.

sec-Octylhydrocupreine dihydrochloride, recommended in Germany during the war, under the name "Vuzin," for the treatment of infected wounds, has also been prepared by the authors.

The values given for the optical rotations are calculated from the formula $[\alpha] = 100\alpha/lc$, c representing grams of substance per 100 c.c. of solvent; for low concentrations, these values are close approximations to the true ones.

The properties of the anhydrous hydrochlorides of the bases are as follows: cinchonine, softens at 175° , m. p. $217\text{--}218^\circ$ (slow decomp.), $[\alpha]_D^{20} + 177.4^\circ$ ($c = 1.083$); cinchonidine, softens at about $160\text{--}170^\circ$, m. p. 242° (slow decomp.), $[\alpha]_D^{20} - 117.6^\circ$ ($c = 1.214$); quinine, melts to a jelly at $154\text{--}160^\circ$, $[\alpha]_D^{20} - 149.8^\circ$ ($c = 1.322$); quinidine, m. p. $258\text{--}259^\circ$ (decomp.) with previous darkening and sintering, $[\alpha]_D^{20} + 200.8^\circ$ ($c = 1.3$); hydroquinidine, m. p. $206\text{--}208^\circ$, $[\alpha]_D^{21} - 123.9^\circ$ ($c = 1.113$); hydrocinchonidine, m. p. $202\text{--}203^\circ$, $[\alpha]_D - 89.4^\circ$ ($c = 1.197$).

Hydrocupreine, prepared as described above, forms faintly cream-coloured plates, and at $185\text{--}190^\circ$ swells and evolves gas, with formation of an adherent, glassy mass, which liquefies completely and darkens at 230° ; $[\alpha]_D^{22} - 148.7^\circ$ ($c = 1.13$) (compare Giemsa and Halberkann, this vol., i, 33). The *hydrochloride*, $C_{18}H_{24}O_2N_2 \cdot HCl$, forms anhydrous, radiating masses of needles, blackening at above 255° , m. p. 280° (decomp.; rapid heating), $[\alpha]_D^{22.5} - 132.3^\circ$ ($c = 0.945$). The dihydrobromide ($+ 2H_2O$) forms leaf-like aggregates of irregular prisms; the anhydrous salt turns yellow and softens to a jelly at about $180\text{--}190^\circ$, gradually liquefying at higher temperatures. The nitrate forms rosettes of anhydrous, flat needles, m. p. $220\text{--}222^\circ$ (darkening).

Ethylhydrocupreine hydrochloride (compare Giemsa and Halberkann, *loc. cit.*) forms anhydrous, rhombic crystals melting at $252\text{--}254^\circ$ to a brown, turbid liquid, which rapidly clears, $[\alpha]_D^{21} - 123.6^\circ$ ($c = 0.959$). The hydrobromide forms aggregates of anhydrous rhombs, m. p. $258\text{--}259^\circ$ (darkening), the dihydrobromide ($+ 0.5H_2O$), greenish-yellow crusts of rhombic crystals, and the methiodide, glistening, pale yellow plates, m. p. $195\text{--}196^\circ$, $[\alpha]_D^{21.5} - 113.0^\circ$ ($c = 0.992$).

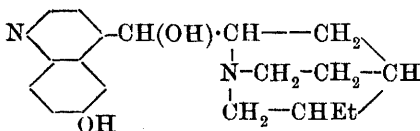
sec-Octylhydrocupreine dihydrochloride ("vuzin") forms pale

yellow sheaves and rosettes of slender needles ($+2\text{H}_2\text{O}$); the anhydrous salt softens slightly above 140° , melts to a jelly at $157\text{--}160^\circ$, and liquefies completely at $190\text{--}195^\circ$ (evolution of gas).

Hydrocinchonine hydrochloride was prepared (1) from the alkaloid occurring naturally as a by-product in the oxidation of commercial cinchonine to cinchotene, and (2) from the base prepared by reducing cinchonine by means of palladium and hydrogen. Both salts ($+2\text{H}_2\text{O}$) conformed to Forst and Böhringer's description (A., 1881, 620). Anhydrous salt (1) darkens above 180° , m. p. $220\text{--}221^\circ$, $[\alpha]_D^{25} + 155.2^\circ$ ($c=0.796$), whilst (2) darkens slightly above 200° , m. p. $221\text{--}223^\circ$ (evolution of gas), $[\alpha]_D^{25} + 159.3^\circ$ ($c=0.741$) (compare von Arlt, A., 1899, i, 962).

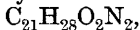
Hydroquinidine hydrochloride (compare Forst and Böhringer, A., 1882, 1306) darkens at about 270° and decomposes at $273\text{--}274^\circ$, $[\alpha]_D^{25} + 183.9^\circ$ ($c=1.278$).

Hydrocupreidine (annexed formula) forms glistening, cream-coloured, hexagonal plates ($+0.5\text{--}1\text{H}_2\text{O}$); the anhydrous base softens to a jelly above 170° and liquefies completely at about 195° , $[\alpha]_D^{19.5} + 253.4^\circ$ (in alcohol; $c=1.422$). In its chemical properties it is strictly analogous to its lævorotatory stereoisomeride.



The *hydrochloride*, $\text{C}_{19}\text{H}_{24}\text{O}_2\text{N}_2\cdot\text{HCl}\cdot\text{H}_2\text{O}$, forms rosettes and sheaves of prismatic needles, and, when anhydrous, has m. p. $231\text{--}233^\circ$ (darkening), $[\alpha]_D^{24} + 194.2^\circ$ ($c=0.618$); its aqueous solution is yellow. The *dihydrobromide* forms anhydrous, pale yellow, glistening plates, and turns yellow when heated, but does not melt at 275° . The *hydriodide* forms pink, rhombic plates ($+\text{H}_2\text{O}$), m. p. $209\text{--}212^\circ$ (anhydrous). The *nitrate* forms cream-coloured rhombs ($+\text{H}_2\text{O}$), the anhydrous salt turning yellow and softening to a jelly at about 160° , and liquefying completely at $175\text{--}180^\circ$. The *methiodide* forms glistening prisms, m. p. about 295° (decomp.), $[\alpha]_D^{20} + 202.6^\circ$ (in 50% alcohol; $c=0.555$).

Ethylhydrocupreidine (ethyl ether of hydrocupreidine),



forms rosettes and sheaves of slender needles, m. p. $197.5\text{--}198^\circ$, showing slight preliminary softening and resolidifying a few degrees below the melting point; $[\alpha]_D^{23.5} + 212.8^\circ$ (in alcohol; $c=1.008$). The *hydrochloride* forms nacreous aggregates of flat needles and long, narrow plates ($+4\text{H}_2\text{O}$) with a slightly bitter taste; the anhydrous salt sinters to a jelly at $140\text{--}155^\circ$, m. p. $258\text{--}260^\circ$, $[\alpha]_D^{23} + 183.3^\circ$ ($c=0.592$). The *hydrobromide* forms anhydrous, rhombic crystals, m. p. $250.5\text{--}253^\circ$ (slow decomp.). The *dihydrobromide* forms radiating masses of slender, silky needles ($+0.5\text{H}_2\text{O}$), the dried salt turning yellow above 130° , melting to a jelly at about $175\text{--}185^\circ$, and swelling and evolving gas at $200\text{--}205^\circ$. The *methiodide* forms rhombs and prisms, decomposing at $253\text{--}255^\circ$, $[\alpha]_D^{23} + 189.6^\circ$ (in methyl alcohol; $c=1.131$).

Quinicine hydrochloride, $\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2\cdot\text{HCl}$, which may readily be

prepared directly from the base, forms arborescent aggregates of minute leaflets, m. p. (1) 179—180°, (2) 180—182°, $[\alpha]_D^{20}$ (1) +16.26° ($c=0.80$), (2) +13.7° ($c=1.861$). T. H. P.

' **Stereochemistry of Hyoscine.** HAROLD KING (T., 1919, 115, 974—982).

Preparation of 6-Hydroxy-2-phenylpyridine-5-carboxylic Acid. CHEMISCHE FABRIK AUF ACTIEN VORM. E. SCHERING (D.R.-P. 312098; from *Chem. Zentr.*, 1919, ii, 852).—The process depends on the oxidation of 2-phenylquinoline bases, substituted in the benzene nucleus, by potassium permanganate in acid solution. Examples are cited of the oxidation of 8-methoxy-2-phenylquinoline, 8-hydroxy-2-phenylquinoline, 6-ethoxy-2-phenylquinoline, m. p. 132° (prepared by heating the corresponding 4-carboxylic acid at 250°), and 6-amino-2-phenylquinoline, m. p. 122—123° (prepared by heating the corresponding 4-carboxylic acid above its melting point). 6-Hydroxy-2-phenylpyridine-5-carboxylic acid (2-phenylpyridone-5-carboxylic acid) forms colourless crystals, m. p. 280—281° (corr.), 287—288° when rapidly heated, and is transformed at 300° into 2-phenylpyridone. A sulphonic acid is produced when it is treated with sulphuric acid containing 15% of SO_3 at 150—160°. The aqueous solutions of the alkali salts are slightly fluorescent. The acid is used medicinally. 6-Hydroxypyridine-2:5-dicarboxylic acid, m. p. 287—289° (decomp.), is obtained as a by-product during the oxidation of 8-methoxy-2-phenylquinoline. H. W.

Dyes Derived from Quinolinic Acid. PRAPHULLA CHANDRA GHOSH (T., 1919, 115, 1102—1105).

Crystallography and Optical Properties of Pinaverdol. EDGAR T. WHERRY and ELLIOT Q. ADAMS (*J. Washington Acad. Sci.*, 1919, 9, 396—405).—Pinaverdol, or 1:1':6'-trimethylisocyanine iodide, is used as a sensitising dye for photographic plates. The crystals are monoclinic ("peri-rhombic") with $a:b:c=1:1.014:1:1.6053$, $\beta=88^\circ 20'$, and they vary from prismatic to tabular in habit in different preparations. They display brilliant reflection pleochroism with metallic colours; faces in the prism-zone are brass-yellow, whilst those nearly perpendicular to the vertical axes are bronze-violet; faces lying between these display intermediate colours, usually a brilliant metallic-green (beetle-green). Crystals less than 0.02 mm. in thickness transmit light and show strong absorption and pleochroism. Refractive indices, α about 1.58, β and γ more than 1.75, probably near 2.0; optically negative. L. J. S.

Isolation of the Iodine Compound which Occurs in Thyroid. E. C. KENDALL (*J. Biol. Chem.*, 1919, 39, 125—147).—Hydrolysis of the fresh thyroid glands is effected with aqueous sodium hydroxide for twenty-four hours. A quantitative separation

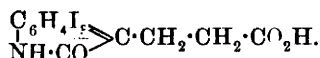
of the fats as sodium soaps is then possible, and a perfectly clear alkaline filtrate of the hydrolysed tissue is obtained. On acidification of this solution, a fine, flocculent precipitate separates which contains approximately 26% of the total iodine. The total iodine is therefore divided into acid-soluble and acid-insoluble fractions. The proportion found in each fraction is remarkably constant, and it is suggested that the ratio expresses the equilibrium existing in the glands between the completed iodine compound possessing physiological activity and the materials which are used by the gland in the building up of this substance. When physiologically tested, the acid-soluble components are inactive, but the small acid-insoluble fraction is highly active.

This fraction apparently consists of a mixture of substances possessing the properties of colloids. As a whole, the fraction possesses acidic properties, and it was ascertained that the iodine compound was not present in the free form. By repeated precipitation with barium hydroxide and removal of the barium as barium sulphate, a preparation containing 47.3% of iodine and nearly free from coloured impurities was obtained. This material was dissolved in 95% alcohol, and on evaporation yielded a white powder insoluble in alcohol and containing about 60% of iodine. When this product was dissolved in aqueous sodium hydroxide, precipitated by adding sulphuric acid, and boiling, it was converted into fine, white, microscopic crystals. This iodine compound has been termed *thyroxin*. The experimental conditions which influence the isolation of thyroxin are fully considered. When an impure preparation of thyroxin is neutralised, iodine is eliminated, but this does not occur as readily when the pure product is used. Thyroxin is very susceptible to reduction in alkaline solution by means of metals.

There are two distinct actions produced by carbon dioxide. One is a partial purification of thyroxin by precipitation from an alkaline solution, whilst the other results in the formation of a mono-metal salt of the closed-ring form of thyroxin.

One of the most important reasons for the failure to separate thyroxin consistently was the variability of the samples of desiccated thyroid used. Samples obtained during the winter months show that during this period the glands are so low in iodine content as to make the isolation impracticable.

The process has been carried out on a large scale, and is fully described. It is stated that the substance is β -4:5:6-tri-iodo-2-keto-4:5:6-trihydroindolepropionic acid,



It may exist in three forms, a keto-form with the carbonyl group adjacent to the imino-group, the tautomeric form with an α -hydroxy-group and doubly linked nitrogen with no hydrogen in position 1, and a form in which there is an open-ring structure. It is stated that the synthesis has been accomplished by Osterberg

in 1917, and that his work has been repeated and confirmed in 1919. No details of the synthesis or of the determination of structure are given.

An acetyl derivative has been prepared. This derivative yielded a disilver salt, and to account for this, rupture of the pyrrole ring between the imino- and the carbonyl groups is assumed to have taken place.

J. C. D.

Capsaicin. I. ARTHUR LAPWORTH and FRANK ALBERT ROYLE (T., 1919, 115, 1109—1116).

Preparation of Nitrogenous Condensation Products of the Anthraquinone Series. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 311906, additional to D.R.-P. 298706; from *Chem. Zentr.*, 1919, ii, 851—852. Compare A., 1918, i, 191).—Thiazole compounds are obtained by treating *o*-halogen-substituted acetylaminanthraquinones with alkali sulphides in accordance with the scheme $A \begin{smallmatrix} \text{NH} \cdot \text{CO} \cdot \text{R} \\ \text{Hal} \end{smallmatrix} + \text{H}_2\text{S} \rightarrow A \begin{smallmatrix} \text{N} \\ \text{S} \end{smallmatrix} \text{C} \cdot \text{R} + \text{H}_2\text{O} + \text{H} \cdot \text{Hal}$, where A represents the anthraquinone group. Thus, *C-phenyl-1:2-anthraquinonethiazole*, pale brown needles, which yield yellow to reddish-brown solutions in organic solvents and yellowish-brown solutions in sulphuric acid, is prepared by boiling 2-bromo-1-benzoylaminoanthraquinone with alcohol and crystalline sodium sulphide. Similarly, 1-chloro-2-acetylaminanthraquinone gives *C-methylantraquinone-2:1-thiazole*, yellowish-green needles, m. p. 258°, which dissolve in organic media and sulphuric acid, forming yellowish-brown and yellow solutions respectively.

H. W.

Reaction of Iodoantipyrine. J. BOUGAULT (*Ann. Chim. anal.*, 1919, [ii], 1, 254; from *Soc. Pharm.*, 1919).—Two atoms of iodine are liberated, and antipyrine (1-phenyl-2:3-dimethyl-5-pyrazolone) is regenerated when an aqueous solution of iodoantipyrine is treated with potassium iodide and hydrochloric acid; this reaction, analogous to that given by hypoiodous amides, indicates that the iodine is combined directly with the nitrogen, although this is not confirmed by the formula ascribed to the substance.

W. P. S.

Pyrimidines. LXXXVII. Alkylation of 5-Aminouracil. TREAT B. JOHNSON and IWAO MATSUO (*J. Amer. Chem. Soc.*, 1919, 41, 782—789).—It has been shown that exhaustive alkylation by means of methyl iodide converts uracil and 5-nitrouracil ultimately into the corresponding 1:3-dimethylpyrimidines. 5-Aminouracil offers, however, greater possibilities of substitution than either of these pyrimidines owing to the presence of the basic amino-group in the 5-position of the ring. Experiment shows that the potassium salt of the aminouracil reacts with methyl iodide at the temperature of boiling methyl alcohol, yielding 5-amino-1:3-dimethyluracil, the substitution occurring entirely in the nucleus of the pyrimidine ring. That substitution does not take place in the

amino-group is established by the fact that, of the four nitrogen-substituted dimethyl derivatives possibly obtainable by alkylation with methyl iodide, neither 5-dimethylaminouracil (compare Wheeler and Jamieson, A., 1904, i, 942) nor 5-methylamino-1-methyluracil nor 5-methylamino-3-methyluracil (see below) is identical with the compound actually obtained.

In the conversion of uracil into 5-nitrouracil, the large excess of nitric acid (D 1.5) is now found to be unnecessary, a theoretical yield being obtained with 4.5 parts of the acid per 1 part of uracil.

5-Amino-1 : 3-dimethyluracil, $\text{CO} \begin{smallmatrix} \text{NMe} \cdot \text{CO} \\ \text{NMe} \cdot \text{CH} \end{smallmatrix} \text{C} \cdot \text{NH}_2$, forms hexagonal plates, m. p. 233—235°, its *hydriodide*, colourless prisms, m. p. 275°, and its *picrate*, yellow needles, melting at 246° to a dark oil with marked effervescence.

5-Methylamino-1-methyluracil, $\text{CO} \begin{smallmatrix} \text{NMe} \cdot \text{CO} \\ \text{NH} \cdot \text{CH} \end{smallmatrix} \text{C} \cdot \text{NHMe}$, obtained from 5-bromo-1-methyluracil and methylamine, forms needles, m. p. 209°, and responds to Wheeler and Johnson's test for uracil (A., 1907, ii, 826); its *picrate* crystallises in long, yellow needles, m. p. 175°.

Alkylation of 2-ethylthiol-6-pyrimidone with methyl iodide under the conditions employed by Johnson and Heyl (A., 1907, i, 728) for the preparation of 2-ethylthiol-1-methyl-6-pyrimidone, followed by hydrolysis by digestion with hydrochloric acid, yields a mixture of uracil, 1-methyluracil, and 3-methyluracil, so that alkylation occurs in both the 1- and 3-positions.

5-Bromo-3-methyluracil, prepared by Johnson and Clapp (A. 1908, i, 835) by the action of bromine on aqueous 3-methylcytosine, may also be obtained in quantitative yield by treatment of 3-methyluracil with bromine in glacial acetic acid solution at the ordinary temperature.

5-Methylamino-3-methyluracil, $\text{CO} \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{NMe} \cdot \text{CH} \end{smallmatrix} \text{C} \cdot \text{NHMe}$, prepared by heating 5-bromo-3-methyluracil with excess of aqueous methylamine solution (33%), forms plates, m. p. 206°.

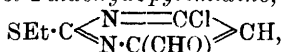
5-Methylaminouracil, $\text{CO} \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{NH} \cdot \text{CH} \end{smallmatrix} \text{C} \cdot \text{NHMe}$, obtained by heating 5-bromouracil (1 mol.) with 33% aqueous methylamine (4 mols.) solution, forms crystals, and, when heated slowly, gradually decomposes without melting; when heated rapidly, it darkens at 285° and melts with violent effervescence at 297°. It gives Wheeler and Johnson's reaction for uracil. Its *picrate* forms stout prisms, m. p. 185° (efferves.).

An attempt to prepare 5-amino-1 : 3-dimethyluracil from 5-nitro-1 : 3-dimethyluracil by reduction with aluminium amalgam in dilute aqueous ammonia gave unsatisfactory results. T. H. P.

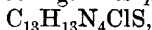
Pyrimidines. LXXXVIII. Synthesis of Cytosine Aldehyde.
TREAT B. JOHNSON and LOUIS A. MIKESKA (*J. Amer. Chem. Soc.*, 1919, 41, 810—817).—The action of phosphorus oxychloride or

pentachloride on 2-ethylthiol-4-aldehydo-6-pyrimidone (compare Johnson and Cretcher, A., 1915, i, 1002) gives, not the expected imide chloride or its chloro-ether, but 6-chloro-2-ethylthiol-4-aldehydopyrimidine. The action of ammonia on this compound results in the replacement of the chlorine atom by an amino-group, but the ammonia reacts also with the aldehyde group, giving 6-amino-4-iminomethyl-2-ethylthiolpyrimidine; hydrolysis of the latter appears to proceed beyond the formation of cytosine-4-aldehyde to the stage of complete reduction of the compound to uracil. A third product of the action of alcoholic ammonia on 6-chloro-2-ethylthiol-4-aldehydopyrimidine is the anhydro-derivative of 6-amino-2-ethylthiol-4-aldehydopyrimidine, this resulting from the inner condensation of the corresponding aldehyde. The 6-amino-2-ethylthiol-4-aldehydopyrimidine was not isolated, but it appears to represent the principal product of the reaction, and, on digestion with hydrochloric acid, is converted into cytosine-4-aldehyde with evolution of ethyl mercaptan.

6-Chloro-2-ethylthiol-4-aldehydopyrimidine,



forms a dark oil, b. p. 138—139°/10 mm., 151—158°/14 mm., solidifying completely on cooling. Its *phenylhydrazone*,



forms long, yellow needles, m. p. 147°, and its *anil*, $\text{C}_{13}\text{H}_{12}\text{N}_3\text{ClS}$, distorted prisms, m. p. 85°.

6-Amino-4-iminomethyl-2-ethylthiolpyrimidine, $\text{SEt} \cdot \text{C} \begin{array}{c} \text{N}=\text{C}(\text{NH}_2) \\ \text{N} \cdot \text{C}(\text{CH} \cdot \text{NH}) \end{array} \text{CH}$, forms prisms, m. p. 182°.

The *inner anhydride* of 6-amino-2-ethylthiol-4-aldehydopyrimidine (annexed formula) forms crystals, m. p. about 210° (decomp.). T. H. P.

Ricinine. E. WINTERSTEIN, J. KELLER, and A. B. WEINHAGEN (*Arch. Pharm.*, 1917, **255**, 513—539).—The formula, $\text{C}_{15}\text{H}_{14}\text{O}_4\text{N}_4$, given by Soave (A., 1896, i, 386) for ricinine must be regarded as erroneous, the results of the authors' analyses and of an investigation of the decomposition products indicating the formula $\text{C}_8\text{H}_8\text{O}_2\text{N}_2$, although ebullioscopic measurements in chloroform, methyl acetate, and pyridine yield values corresponding with $\text{C}_{12}\text{H}_{13}\text{O}_3\text{N}_3$; no explanation of this discrepancy is advanced. The compound, $\text{C}_8\text{H}_8\text{O}_2\text{N}_2 \cdot \text{HgCl}_2$, m. p. 201—202°, Soave (*loc. cit.*) described as $\text{C}_{17}\text{H}_{13}\text{O}_2\text{N}_2 \cdot 2\text{HgCl}_2$, m. p. 204°.

Ricinine is readily hydrolysed by alkalis, yielding methyl alcohol and the sparingly soluble ricinic acid, $\text{C}_7\text{H}_6\text{O}_2\text{N}_2$, m. p. 292°; Soave gave m. p. 295°, and Maquenne and Philippe (A., 1904, i, 339; 1905, i, 80) m. p. 320°, which is that of the sodium salt. One hundred grams of water dissolve 0.072 gram of the acid at 18° and 0.87 gram at 100°. The *silver* (+ H_2O) and *barium* salts were prepared and analysed. Ricinic acid is optically inactive,

and attempts to esterify it were unsuccessful. Treatment of ricinine with a small proportion of permanganate results in hydrolysis accompanied by oxidation of the methyl alcohol liberated, whilst, when excess of permanganate is used, ammonia, hydrocyanic, oxalic, and succinic acids are formed, together with other products not investigated.

When distilled with zinc dust, ricinine gives pyridine and other compounds, and when fused with potassium hydroxide, aliphatic amines. Towards ordinary reducing agents, ricinine exhibits considerable stability, but by hydrogen in presence of platinum black it is slowly converted into tetrahydricinine, $C_8H_{12}O_2N_2$, which is far less poisonous than ricinine and forms a readily soluble, crystalline *hydrochloride*, $C_8H_{12}O_2N_2 \cdot HCl$, m. p. 212—215°, a crystalline *platinichloride*, $(C_8H_{12}O_2N_2)_2 \cdot H_2PtCl_6$, decomposing at about 222—225°, and an *aurichloride*, $C_8H_{12}O_2N_2 \cdot HAuCl_4$, sparingly soluble in water. Tetrahydricinine gives precipitates with a large number of alkaloid reagents. Hydrogenation of ricinic acid yields methylamine.

When heated with concentrated hydrochloric acid at 145°, both ricinine and ricinic acid yield ammonia and the base, $C_6H_7O_2N$ (compare Maquenne and Philippe, *loc. cit.*), which is also obtained by the action of 57.4% sulphuric acid on ricinic acid at 140°. Under the latter conditions, ricinine gives a *base*, $C_7H_9O_2N$ ($+ 3H_2O$), which crystallises in shining, felted needles, m. p. 55—57° or 112—114° (anhydrous), and yields a *platinichloride*, $(C_7H_9O_2N)_2 \cdot H_2PtCl_6$, m. p. 198—199°, an *aurichloride*, $(C_7H_9O_2N)_2 \cdot HAuCl_4 \cdot H_2O$,

m. p. 129—131° (dried in a vacuum), and a *bromine* additive compound, m. p. 95° or 110° (dry); various reactions of this base, which exhibits normal cryoscopic behaviour in water, are described. The decomposition of ricinine by sulphuric acid is expressed by the equation $C_8H_8O_2N_2 + 2H_2O = NH_3 + CO_2 + C_7H_9O_2N$, and that of ricinic acid by $C_7H_8O_2N_2 + 2H_2O = NH_3 + CO_2 + C_6H_7O_2N$.

Both ricinine and the base, $C_7H_9O_2N$, contain one methoxy-group in the molecule; the former yields neither a benzoyl nor an acetyl compound, but with bromine it gives the *bromo*-derivative, $C_8H_7O_2N_2Br$, m. p. 226—230° (compare Evans, A., 1900, i, 309; Soave, *loc. cit.*). Ricinic acid cannot be converted into ricinine by the ordinary methods of methylation.

Since, under certain experimental conditions, ricinine gives Weidel's and the murexide reactions, it is possible that its molecule contains a pyrimidine ring.

T. H. P.

Vicine. I. E. WINTERSTEIN (*Zeitsch. physiol. Chem.*, 1919, 105, 258—264. Compare Levene, A., 1914, i, 1004).—The author's preparation had m. p. 239—242° (decomp.). A 10% solution in 10% sulphuric acid had $[\alpha]_D^{15} - 8.77^\circ$, whilst a 6.6% solution in *N*/5-sodium hydroxide gave $[\alpha]_D - 12.1^\circ$. On hydrolysis with *N*-sulphuric acid, it yielded 59.3% and 60.05% of a sugar,

identified definitely as dextrose. The elementary analysis corresponded with $C_{10}H_{16}O_7N_4$. J. C. D.

Abnormal Behaviour of Glyoxalinecarboxylic Esters and Anilides towards Diazonium Salts. ROBERT GEORGE FARGHER and FRANK LEE PYMAN (T., 1919, 115, 1015—1020).

Partition of the Benzene Derivatives and the Benzene Carbon in the Protein Molecule. E. and H. SALKOWSKI (*Zeitsch. physiol. Chem.*, 1919, 105, 242—248).—An attempt to gain information as to the partition of the cyclic amino-acids in proteins by a study of their degradation products formed during putrefaction. From putrefied fibrin there were isolated 1·26% of indole, either in the free form or as indoleacetic acid, 2·85% of phenol, free or as hydroxy-acids, and 1·27% of β -phenylpropionic acid. A study of these quantities throws light on the amounts of tyrosine, tryptophan, and phenylalanine originally present in the fibrin, and it is suggested that such studies might be of value in determining the biological value of proteins. J. C. D.

Preparation of Protein Free from Water-soluble Vitamine. THOMAS B. OSBORNE, ALFRED J. WAKEMAN, and EDNA L. FERRY (*J. Biol. Chem.*, 1919, 39, 35—46).—The persistence with which the water-soluble vitamine is retained by edestin suggests that it is chemically combined therewith. Caseinogen, lactalbumin, gliadin, and ovovitellin as prepared by the usual methods do not appear to carry this vitamine as an impurity. The water-soluble vitamine present in yeast is not entirely destroyed by digestion with 0·1*N*-sodium hydroxide for twenty-one and a-half hours, followed by heating on the water-bath for two hours. J. C. D.

Effect of Various Acids on the Digestion of Proteins by Pepsin. J. H. NORTHRUP (*J. Gen. Physiol.*, 1919, 1, 607—612).—The rate of digestion of gelatin, egg-albumin, edestin, blood-albumin, and caseinogen by pepsin in the presence of hydrochloric, nitric, acetic, sulphuric, oxalic, phosphoric, and citric acids was followed by measuring the increase in free amino-groups by the method of Van Slyke (A., 1913, ii, 1084). The estimations were made at two ranges of hydrogen-ion concentration, $p_H=1\cdot0$ to $1\cdot5$ and $p_H=2\cdot5$ to $3\cdot5$. The rate of hydrolysis of all the proteins studied was found to be identical for all the acids except acetic acid. These experiments show that the physical properties of the solution, such as viscosity, have little or no effect on the rate of digestion. The simplest explanation of the results would seem to be that the rate of digestion of the protein is determined by the amount of acid protein salt formed. J. C. D.

The Proteins of Fenugreek Seeds. H. E. WUNSCHENDORFF (*J. Pharm. Chim.*, 1919, [vii], 20, 86—88).—Fenugreek seeds contain 27% of proteins; the latter consist of globulin, 25%; two albumins, 20%; and a nucleoprotein, 55%. The nucleoprotein is rich in iron (3·99%) and phosphorus (1·58%); on hydrolysis with

10% hydrochloric acid for two hours at 100°, it yields alanine 1·6%, leucine 2·50%, phenylalanine 2·5%, glutamic acid 35·71%, aspartic acid 1·32%, tyrosine 4·65%, arginine 3·15%, histidine 0·75%, proline 3·80%, glycine and lysine none. A solution of the substance in alkali hydroxide has $[\alpha]_D -97.7^\circ$. W. P. S.

Salmine. MATHILDE NELSON-GERHARDT (*Zeitsch. physiol. Chem.*, 1919, **105**, 265—282).—The author has found that there is an increase in acidity on hydrolysis of salmine similar to that observed by Goto in the hydrolysis of clupeine (A., 1903, i, 303). The cause of this increase is discussed. Sørensen's explanation ("Ergebnisse der Physiologie," 1912), based on the keto-enol tautomerism of the peptide linkings, demands that the original acidity returns when all these linkings are broken. This theory holds in the case of certain examples, such as glycine anhydride and leucylglycine. If it is to apply to the hydrolysis of salmine, it is necessary to assume that the process ceases before all the peptides are resolved. On investigation, peptides of the monoamino-acids were found to be present, and when the hydrolysis was completed by decomposition of these complexes, the acidity returned to the original value.

There is, however, evidence of another cause of increased acidity. Search for a new dibasic monoamino-acid was unsuccessful. Other possible causes are considered. J. C. D.

Bacterial Catalase. III. MARTIN JACOBY (*Biochem. Zeitsch.*, 1919, **95**, 124—130).—The preparation of a highly active catalase fraction from *Bacillus proteus* is described. J. C. D.

Studies on Lipase. GEN-ITSU KITA and MINORU OSUMI (*J. Tokyo Chem. Soc.*, 1918, **39**, 387—422).—On account of discrepancy among various workers on the question of relationship between acid and lipase, the authors conducted extensive studies on (1) the medium for the lipolytic enzyme, (2) optimum concentrations of the different acids for activation of the zymogen, (3) the effect of washing, and (4) the effect of alcohol, water, and various other substances. This paper is partly polemical with regard to Tanaka's paper (*ibid.*, **34**, 737). Castor beans are used for the source of lipase and soja-bean oil for the substratum. The results confirm Hoyer's work that the function of acid is solely to activate the zymogen, and the activated lipase can act without the addition of any acid, but after repeated washing a little addition of an acid will accelerate the reaction. Sensitivity of activated lipase against an acid depends entirely on the amount of the oil present in the medium. If activated lipase is left in an acid without any oil and then later the oil is added, no hydrolysis will take place, whereas if the oil and the enzyme are put together from the beginning, the hydrolysis will occur even to the extent of 80%. The optimum concentration of various acids for activation varies according to the kind of acid used, the stronger acids requiring fewer c.c. of normal solution than weaker acids, but the extent of hydro-

lysis is always greater with the weaker acid. Using 2.5 grams of the castor beans + 25 grams of the oil + 5 c.c. of water (including c.c. of the acid used), incubating at 39° for three hours, the amount of *N*-nitric acid necessary to give the maximal hydrolysis (32.9%) is 0.6 c.c.; for *N*-sulphuric acid, 0.75 c.c. The maximal digestion being 37%; for *N*-oxalic acid, 0.75 c.c., giving 36.8%; 0.75 c.c. of *N*-tartaric acid gives 41.8%; 1 c.c. *N*-lactic acid, 41.5%; 1.5 c.c. *N*-citric acid, 56.2%; 4 c.c. of *N*-succinic acid, 45.97%; and 3 c.c. of *N*-acetic acid, 54.4%. In making a permanent lipase preparation, the optimum amount of acids should be added according to (1) the amount of the oil the seed contains, the greater the amount of the oil the smaller the number needed; (2) the size of the crushed beans, the smaller the granules the less the amount of the acid needed; (3) temperature, the higher the less amount of acid; and (4) time, the longer the treatment the less the acid necessary. Dilution of the acid, maintaining in the medium the absolute amount of the acid necessary for the maximal amount of hydrolysis, lessens the lipolytic power, especially in the case of strong acids. The strong acids once used for activation of zymogen will have no effect for activating a new bean, but the weak acids will. When the castor bean is washed with water containing sodium or calcium chloride, its enzymic power is reduced, probably by loss of globulin. Addition of acetic acid will counteract this salt effect. Unlike other enzymes, lipase is exceedingly sensitive to alcohol, but ether, benzene, and carbon disulphide will not destroy it. Lipase in aqueous solution loses its activity very quickly if no oil is present.

CHEMICAL ABSTRACTS.

Manufacture of the Organic Phosphorus Reserve Compound of Green Plants, and Salts Thereof. SOCIETY OF CHEMICAL INDUSTRY IN BASLE (Brit. Pat., 130456).—A pure sodium salt of the organic phosphorus reserve compound is prepared from the impure material through the intermediate precipitation of the ferric salt, its decomposition by sodium hydroxide, and the addition of alcohol to the filtered solution. The crystalline mass which separates gives on recrystallisation from water efflorescent prisms of the composition $C_6H_6O_{24}P_6Na_{12} \cdot 47H_2O$, m. p. 49°. The anhydrous salt is a stable, white, non-hygroscopic powder, alkaline in reaction and insoluble in organic solvents. Pure alkaline earth, lead, and copper salts are obtained by double decomposition, and from them the pure acid of the phosphorus compound is prepared by the action of oxalic acid or hydrogen sulphide, as the case may be. [See, further, *J. Soc. Chem. Ind.*, 1919, 739A.] G. F. M.

Cytidine-Phosphoric Acid. P. A. LEVENE (*J. Biol. Chem.*, 1919, 39, 77—81. Compare A., 1918, i, 138).—The preparation of the pure brucine salt of cytidine-phosphoric acid is described. From this may be prepared the barium salt, $C_9H_{12}O_8N_3PBa$. The optical rotation of the air-dried substance was $[\alpha]_D^{20} + 14.0^\circ$. By hydrolysis of the barium salt by heating with 10% sulphuric acid

in a sealed tube at 125°, cytidine was formed, where cytosine had been expected. No explanation of this result is given. No uridine was found in the mother liquors from the cytidine picrate.

J. C. D.

Sodium Inositol-hexaphosphate (a Correction). S. POSTERNAK (*Compt. rend.*, 1919, 169, 337—338. Compare this vol., i, 426).—A stable form of this compound containing only 35 mols. H_2O is slowly deposited from concentrated solution at about 20°. It melts at 58—59° and loses water of crystallisation at 120°, and the crystallographic measurements recently given (this vol., i, 426, 433) refer to this substance and not to the efflorescent hydrate containing 44 mols. H_2O .

G. F. M.

Substituted Phenylarsinic Acids and their Reduction Products, and the Estimation of Arsenic in such Compounds. ROBERT GEORGE FARGHER (T., 1919, 115, 982—992).

Formaldehyde Derivative of Arsenophenylglycine. K. J. OECHSLIN (U.S. Pat. 1299214).—Arsenophenylglycine is dissolved in a 6% solution of sodium carbonate and treated with formaldehyde. On the addition of alcohol or acetone to the solution, a sodium salt of the reaction product is obtained, which possesses a light yellow colour, and may be dried and kept in the air for some time without decomposition.

CHEMICAL ABSTRACTS.

Acetylarsenophenylglycine. K. J. OECHSLIN (U.S. Pat. 1299215).—A solution of acetylphenylglycinearsinic acid (50 grams) and sodium hyposulphite (500 grams) in water (2500 c.c.) is heated for two hours at 45—55°, and acetic acid (70 c.c.) is then added. Acetylarsenophenylglycine is precipitated in light yellow flakes. Acetylarsenophenylglycine also may be prepared by dissolving arsenophenylglycine in sodium carbonate solution and successively adding acetic anhydride and hydrochloric acid.

CHEMICAL ABSTRACTS.

Physiological Chemistry.

Absorption of Light by Neutral Solutions of Oxyhæmoglobin. PAUL HARI (*Biochem. Zeitsch.*, 1919, 95, 257—265).—The absorption of light by neutral solutions of blood or of oxyhæmoglobin is very little different from that of solutions in aqueous sodium carbonate. The difference is attributed to the presence of small amounts of methæmoglobin.

J. C. D.

Behaviour of Inulin in the Animal Body. II. Inulin in the Alimentary Canal. RUTH OKEY (*J. Biol. Chem.*, 1919, **39**, 149—162).—Inulin is hydrolysed in vitro by hydrochloric acid of a concentration approximately the same as that in the normal gastric juice provided a sufficiently long period of hydrolysis is allowed. During the time normally occupied by food in the stomach, the amount of hydrolysis is comparatively small. The presence of an enzyme capable of producing a reducing sugar from inulin has been demonstrated in sterile extracts of three samples of human faeces from radically different types of diet. Negative results were obtained with samples from a dog and guinea-pigs.

J. C. D.

Genesis of Thiocyanic Acid in Animals. VII. From what Substances is Normal Thiocyanic Acid Derived in Animals? SERAFINO DEZANI (*Arch. Farm. speriment. sci. aff.*, 1918, **26**, 257—273; from *Chem. Zentr.*, 1919, iii, 65. Compare this vol., i, 423).—The negative results obtained with amino-acids and derivatives of purine in the case of the dog are in contrast with the positive results of Willanen (A., 1906, ii, 784) in the case of the rabbit. The latter experiments have been repeated, particular attention being given to the influence of the nourishment. No increase in thiocyanic acid could be detected after administration of glycine, asparagine, guanine, or creatinine; evidence in favour of the hypotheses of Nencki and of Bruylants is therefore not obtained.

H. W.

Quinine and Hydroquinine in the Human Body. Behaviour of Quinine towards Red Blood Cells. J. HALBERKANN (*Biochem. Zeitsch.*, 1919, **95**, 24—45).—The fate of these two substances in the body is discussed. It is shown that quinine may be taken up and retained by the erythrocytes.

J. C. D.

Presence of Histamine (β -Iminazolyethylamine) in the Hypophysis Cerebri and Other Tissues of the Body and its Occurrence Among the Hydrolytic Decomposition Products of Proteins. JOHN J. ABEL and SEIKO KUBOTA (*J. Pharm. Expt. Ther.*, 1919, **13**, 243—300).—The experimental findings support the view previously expressed (*Proc. Nat. Acad. Sci.*, 1917, **3**, 507—517) that the oxytoxic principle of the hypophysis is not a hormone or substance specific to this organ, but is a rather widely distributed substance, everywhere the same, which may have its origin in the various tissues or in the gastric or intestinal mucosa, or may be absorbed as such from among the products of digestion. This substance is now believed to be histamine, a substance which stimulates plain muscle in minute doses and which depresses the circulation and causes a shock-like prostration when administered in doses which lie beyond the limit of toleration. The base was isolated with certainty from pituitary tissue and gastric and intestinal mucosa of the dog, and its presence in liver tissue and striated muscle was detected. The amine was also found in erepton (com-

pletely digested meat), Witte's peptone, and amongst the products of hydrolysis of pure proteins with hydrochloric acid. It is suggested that histamine plays an important rôle as a stimulant for the gastric and intestinal musculature and as a dilator of capillaries during digestion. J. C. D.

[Physiological Action of] Optical Isomerides. V. The Tropeines. A. R. CUSHNY (*J. Pharm. Expt. Ther.*, 1919, 13, 71—93. Compare A., 1909, ii, 420).—Atropine is twenty times as strong as *d*-hyoscyamine in affecting the terminations of the chorda tympani in the dog. Therefore *l*-hyoscyamine would have an action forty times as great as that of its optical isomeride. The difference between the effects of atropine and *d*-hyoscyamine on cardiac inhibition is of the same order as on salivary secretion. The physiological action of a number of tropeines has been examined. Tropine itself is devoid of typical atropine action, but many tropeines, especially those which contain a benzene nucleus, show the characteristic effects. This is particularly intensified where there is a hydroxyl group or an asymmetric carbon atom in the side-chain. The most powerful action is shown by members of this type which contain an acid of the benzene series, together with a hydroxyl group and asymmetric carbon atom in the side-chain, and the whole molecule of which is lævorotatory. J. C. D.

Vitamine Studies. IV. Antineuritic Properties of Certain Physiological Stimulants. R. ADAMS DUTCHER (*J. Biol. Chem.*, 1919, 39, 63—68).—Thyroxin (the active principle of the thyroid), desiccated thyroid, pilocarpine, and tethelin apparently produced definite relief in certain acute cases of avian polyneuritis. The response was not, however, of the type obtained when vitamine preparations were given. J. C. D.

Chemistry of Vegetable Physiology and Agriculture.

Biochemistry of *Bacillus Acetoethylicum* with Reference to the Formation of Acetone. JOHN H. NORTHROP, LAUREN H. ASHE, and JAMES K. SENIOR (*J. Biol. Chem.*, 1919, **39**, 1—21).—The description of an organism termed *Bacillus acetoethylicum* which was isolated from old potatoes is given. The organism resembles in some ways the *B. macerans* described by Schardinger (*Centr. Bakt. Par.*, 1905, ii, **14**, 772), but it is not thought that the two are identical. This organism produces acetone and ethyl alcohol from starch or sugar. The optimum conditions for the fermentation have been studied, and a semi-continuous method for carrying on the process is described. [See, further, *J. Soc. Chem. Ind.*, 1919, October.] J. C. D.

Formation of Acids by Moulds and Yeast. III. FRIEDRICH BOAS and HANS LEBERLE (*Biochem. Zeitsch.*, 1919, **95**, 170—178. Compare *ibid.*, 1918, **90**, 78; **92**, 171).—When both ammonium sulphate and acetamide are present as sources of nitrogen for *Aspergillus niger* growing in an artificial culture solution, only the ammonium sulphate is utilised, notwithstanding that acetamide would from some point of view appear a more suitable material for protein synthesis, particularly as its utilisation does not necessitate the liberation of a toxic substance, such as the sulphuric acid liberated in the utilisation of ammonium sulphate. From similar tests with glycine and acetamide, it would appear the glycine is utilised, whereas the amide is almost untouched. Experiments in which the mould has a choice between ammonium sulphate and peptone show that preferential utilisation of the former source of nitrogen occurs. In fact, when *A. niger* is given the choice between two sources of nitrogen, one of which is an ammonium salt and a strong mineral acid, it utilises the ammonium salt alone, in spite of the fact that this leads to a rise of hydrogen-ion concentration with all its deleterious consequences.

Apparently the degree of dissociation of the ammonium salt is an important factor. J. C. D.

The Formation of Soluble Starch in Relationship to Selective Nitrogen Metabolism. FRIEDRICH BOAS (*Ber. Deut. bot. Ges.*, 1919, **37**, 50—56).—It has been previously shown that soluble starch is formed from many carbohydrates by *Aspergillus niger* when the hydrogen-ion concentration has attained a certain value. The author has based a method of studying selective nitrogen metabolism on this observation; thus, for instance, when in a sugar solution ammonium chloride is consumed in addition to amino-acids, the hydrogen-ion concentration rapidly increases in consequence of the liberation of the greatly dissociated hydrochloric acid, so that favourable conditions are developed for the formation of soluble starch, which can readily be detected by the iodine test. The following groups have been studied: mixtures of ammonium salts (ammonium chloride and ammonium phosphate or citrate); amino-acids and peptones in the presence of ammonium chloride; acid amides (carbamide) and ammonium chloride. The latter differs from all the other sources of nitrogen which were investigated in that it is strongly dissociated. Experiments show that in mixtures of nitrogenous substances with varying degrees of dissociation, the magnitude of the latter determines the absorption into the cell. In comparison, the solubility of the substance in lipoids has but little influence. The more strongly dissociated source of nitrogen is invariably utilised even when powerfully poisonous products are thereby developed, and when other non-poisonous, lipid-soluble and suitable sources of nitrogen are present. Absorption is not regulated by the mould, but occurs exclusively according to physico-chemical properties. From the biological point of view, the mould invariably utilises the worse source of nitrogen. H. W.

Parallel Formation of Carbon Dioxide, Ammonia, and Nitrate in Soil. P. L. GAINES (*Soil Sci.*, 1919, 7, 293—311).—

In laboratory experiments, purified air was drawn in a downward direction through a column of loam soil supported in a cylinder, and then through glass beads moistened with a solution of sodium hydroxide, and afterwards through glass beads moistened with dilute acid. Usually, six of these apparatus were connected in series. Estimations of the carbon dioxide and ammonia retained by the absorption vessels determined the amounts of these gases given off, and after each experiment the top layer of soil was removed and examined for ammonia and nitrates. The carbon dioxide in the soil was not taken into consideration. One per cent. of cotton-seed meal was added to the soil as a substance readily decomposed by bacteria. Observations on variation in the moisture content of the soil showed that this factor had little effect on the carbon dioxide evolved provided the amount of water was above a minimum of 12 c.c. per 100 grams of soil. The maximum amount of carbon dioxide was produced during the second day. The production of ammonia ran parallel with that of carbon dioxide, except that the optimum minimum of moisture was rather higher. The accumulation of nitrates did not begin until the fifth day, and the amount increased regularly with a corresponding diminution in that of the ammonia. Variations in air supply had a marked effect on bacterial activity. Unless the current of air was continuous, there was a distinct diminution and delay in the changes produced. In the case of ammonia, there was a permanent diminution in amount; in the other two cases, the amount of carbon dioxide finally reached that produced in continuous aeration, whilst the amount of nitrate became inversely proportional to aeration. Experiments were made also with 1% of dried blood added to the soil. With this substance, the production of carbon dioxide was much diminished and that of ammonia relatively increased, probably due to the higher nitrogen content of the blood over the cotton-seed meal and to the amount of readily oxidisable carbon being insufficient to supply energy for complete decomposition.

J. H. J.

Action of Capillary-active Substances on Plant Seeds.

I. TRAUBE and HEDWIG ROSENSTEIN (*Biochem. Zeitsch.*, 1919, 95, 85—100. Compare Traube and Marusawa, A., 1916, i, 106).—The influence of a large number of substances on the germination and growth of seeds has been investigated. Narcotics, such as chloroform, ether, and urethane, produce a narcotic action which is in certain respects similar to the effect on the animal organism. Many substances, such as toluene, chlorobenzene, piperidine, pyridine, aniline, acetone, isobutyl acetate, and isoamyl alcohol are strongly toxic. Naphthalene and thymol vapour may hasten germination if the exposure is not too long, whilst *m*-cresol may in certain concentrations beneficially influence the growth of barley.

The higher fatty acids exert a marked stimulating action on the

rate of germination, whereas the lower fatty acids in low concentrations are very poisonous. J. C. D.

The Opposed Action, Antagonism, of Manganese and Iron on the Growth of Wheat. W. E. TOTTINGHAM and A. J. BECK (*Plant World*, 19, 359—370; from *Chem. Zentr.*, 1919, iii, 110).—Small quantities of manganese chloride are harmful to the root system and inhibit the positive action of ferric chloride. Both salts are poisonous at greater concentrations, at which the ferric chloride restricts the action of manganese chloride. Small quantities of manganese chloride induce more rapid growth of the plant, but the same antagonism is observed as with the root system. In the presence of sodium hydrogen carbonate, manganese chloride is disadvantageous to the roots and green parts even in small amounts, and distinctly poisonous at higher concentrations. Contrary to previous observations, ferric chloride encourages the growth of terminal shoots, probably on account of the alkaline nature of the nutrient solution. H. W.

The Alkaloids in Plant Injury. O. TUNMANN (*Biochem. Zeitsch.*, 1919, 95, 164—169).—No accumulation of alkaloid was found to follow injury to the leaves of *Atropa belladonna*, L., or *Pilocarpus pennatifolius*, Lem., whether caused by animals or by artificial methods. This is not in agreement with the work of Troegele (*Diss.*, Würzburg, 1900). J. C. D.

Nutritive Factors in Plant Tissues. II. The Distribution of the Water-soluble Vitamine. THOMAS B. OSBORNE and LAFAYETTE B. MENDEL (*J. Biol. Chem.*, 1919, 39, 29—34).—The water-soluble vitamine is present in the bulb of the onion, the root of the turnip, the leaves, stem, and roots of the beet, and the fruit of the tomato. A comparison of mature and immature plants of clover, lucerne, and timothy grass indicates that the immature plants are the richer sources of water-soluble B. The bearing of this observation on the food value of hay is discussed. J. C. D.

Relation of Sulphates to Plant Growth and Composition. H. G. MILLER (*J. Agric. Res.*, 1919, 17, 87—102).—Pot experiments were made with three soils, one selected for its high content of sulphur, namely, 0.183%, one because it had responded to free sulphur treatment, and one because it did not respond to any sulphur treatment. The plants grown were red clover, oats, and rape. The fertilisers used were calcium and sodium sulphates and free sulphur. The last was added with calcium carbonate to the soil at the time of sowing the seed; the other two were added daily in the form of 0.02% solutions. A solution of sodium nitrate was added daily in order to provide excess of nitrogen in every case. A similar set of experiments was made in which the soil was replaced by washed sand, to which was added a sterilised extract of the soil. The weight of the crops was noted, and the content of sulphur and

nitrogen estimated. It was found in every case that enhanced growth took place as compared with the control tests, especially marked in the case of the oats and clover. As this enhanced growth took place in the sand as well as in the soil, it is concluded that the sulphates and free sulphur acted directly in the promotion of growth. In the case of clover, there was a marked increase in the nitrogen content of those plants grown in soil over those grown in sand, doubtless due to stimulation of the legume bacteria by the fertilisers added, as was evidenced by the increased root development and number of nodules in these cases.

J. H. J.

Nitrogen and Other Compounds in Rain and Snow.

JACOB E. TRIESCHMANN (*Chem. News*, 1919, 119, 49).—A summary of the analyses of forty-six samples of rain and snow collected at Cornell between October 1st, 1918, and June 15th, 1919, is given. The total precipitation corresponds with 56·3 cm. of rain, and contained 572 kilos. of chlorine (944 kilos. of sodium chloride), 1·679 kilos. of sulphates as SO_3 , and 5·853 kilos. of nitrates per hectare. The phosphates only amounted to 0·0089 kilos. per hectare. Only fifteen samples contained sufficient sulphate for analysis, and eleven other samples showed the merest trace of sulphate. The highest sulphate content was 0·262 part per million, the average for the period being 0·03 part per million. Five samples showed a trace of phosphate, but only four contained sufficient for estimation. The highest content of phosphate was 0·03 part per million, the average being 0·002 part per million. The chlorine content averages 11·12 parts per million, and varies between 6·10 and 25·70 parts per million. The average of the total nitrogen was 1·046 parts per million. The free ammonia is represented by 0·407, albuminoid ammonia 0·366, nitrate 0·255, and nitrite 0·018 part per million. The total nitrogen is fairly constant, and forty-three of the forty-six determinations lie between 0·18—0·45 kilos. of nitrogen per hectare. The amount of nitrogen increased from 0·669 part per million to 1·134 parts per million from February to June, that is, an increased amount of nitrogen is supplied to the soil during the growing period.

J. F. S.

Ammonia-fixing Capacity of Calcium Sulphate.

FIRMAN E. BEAR and ALBERT C. WORKMAN (*Soil Sci.*, 1919, 7, 283—291).—It has been observed that the addition of calcium sulphate to manure tends to prevent loss of ammonia. To test the nature of this reaction under simple conditions, laboratory experiments were carried out in which the manure was replaced by paper pulp, which was mixed with calcium sulphate and placed in a bottle. A solution of ammonium carbonate was poured over the pulp, giving a water content of 75%. The bottle was kept at different temperatures from 20° to 80°. A current of air freed from ammonia and carbon dioxide was drawn through the mixture in the bottle, and then through absorption vessels containing standard

acid. Observations were continued over ninety-five days, air being drawn through about daily for ten minutes at a time. The nitrogen loss without calcium sulphate was 5.6225 grams, and with calcium sulphate 1.1419 grams. More nitrogen was lost at the higher temperatures, and the proportion held back by the calcium sulphate was less at those temperatures. Under the conditions of the experiment, the chemical reaction was probably that of a simple double decomposition. [See also *J. Soc. Chem. Ind.*, 1919, 731A.]

J. H. J.

Electrical Conductivity as a Measure of the Content of Electrolytes of Vegetable Saps. DOROTHY HAYNES (*Biochem. J.*, 1919, 13, 111—123).—The causes of the low values obtained in conductivity measurements in fruit juices containing considerable quantities of organic acids are submitted to examination. These low figures are due to two principal causes, first, the action of non-electrolyte (compare Arrhenius, A., 1892, 1038), and secondly, the mutual action of salts and acids in repressing dissociation. The conclusions of Dixon and Atkins (A., 1913, i, 1422) drawn from a comparison between the juice from plant organs when pressed without previous treatment and the juice of the same organs when treated by exposure to liquid air before pressing are criticised. It is suggested that there is very little evidence for the marked differences which they assume to exist in the proportional composition of the two kinds of sap. It is further suggested that these experiments afford no evidence that the protoplasm of the cells of tissue under pressure is permeable to electrolytes to any considerable extent. A formula is advanced by means of which, in certain cases, conductivity measurements may be reduced to standard conditions.

J. C. D.

Examination of the Bark of Croton gubouga. Isolation of 4-Hydroxyhygric Acid. JOHN AUGUSTUS GOODSON and HUBERT WILLIAM BENTLEY CLEWER (*T.*, 1919, 115, 923—933).

Action of Fluorides on Vegetation. B. Field Trials. ARMAND GAUTIER and P. CLAUSMANN (*Compt. rend.*, 1919, 169, 115—122).—As the result of field trials, using amorphous calcium fluoride as the source of fluorine, the authors find that this element increases the crop yield in certain species of plants. The calcium fluoride was applied at the rate of 55.8 grams per sq. metre to a poor, sandy soil. Increased crop yields varying from 5.2 to 58.7% were obtained with wheat, oats, carrots, potatoes, peas, beans, and poppies, whilst beet, kidney beans, and cabbage gave either no increase or a decrease. In the case of potatoes, there was no marked increase in the yield in the year of application of the calcium fluoride, but a very decided increase (58.7%) in the next year. Most of the other crops showed little, if any, residual effect in the second year.

W. G.

Organic Chemistry.

The Action of Cuprous Chloride with Compounds containing the Trichloromethyl Group. HOWARD WATERS DOUGHTY (*J. Amer. Chem. Soc.*, 1919, **41**, 1129—1131).—As an outcome of his work on the hydrolysis of organic haloids and the corrosion of metals (A., 1918, i, 57), the author recommends the following procedure as a test for the presence of compounds containing the CCl_3 or CBr_3 groups. A few milligrams of the substance are placed in a stoppered vessel of 10—15 c.c. capacity, which is then filled with concentrated ammonia solution. About 0.5 gram of powdered cuprous chloride is then added, and the vessel is quickly closed to exclude air, and shaken. The deep blue colour of the cupric-ammonia complex develops in a minute or two if a trichloro- or tribromo-methyl group is present. Carbon tetrachloride behaves in the same way, but hexachloroethane does not respond J. C. W.

Preparation of Trichloroethylene from Tetrachloroethane. COMPAGNIE DES PRODUITS CHIMIQUES D'ALAIS ET DE LA CAMARGUE (Eng. Pat., 132755).—The conversion of *s*-tetrachloroethane into trichloroethylene may be effected by ammonia in aqueous solution provided that a sufficient time be allowed for the reaction. A mixture of equal parts of water and tetrachloroethane is treated in a vessel provided with a reflux condenser with a current of ammonia gas sufficiently violent to agitate the mass. The reaction takes place slowly in the cold, and is accelerated by heating at 60—70°; it is complete in two hours if the trichloroethylene is removed as it is formed by extracting it with an excess of ammonia gas and adjusting the temperature of the condenser in accordance with this excess. The reaction may also be conducted in an autoclave by heating two parts of tetrachloroethane with two parts of an aqueous solution of ammonia (D 0.91) at 140—170° for three hours. The use of aqueous ammonia is simpler and more economical than that of alcoholic ammonia, and the yield of trichloroethylene is 92—96% of the theoretical. J. F. B.

Vapour Pressure of Tetranitromethane. ALAN W. C. MENZIES (*J. Amer. Chem. Soc.*, 1919, **41**, 1336—1337).—The vapour pressure of tetranitromethane has been determined by a static isoteniscopic method, previously described (A., 1910, ii, 1036), over the temperature range 40—125.7°. The following values were obtained in mm. of mercury: 40°, 26.6; 45°, 34.4; 50°, 44.2; 55°, 56.1; 60°, 70.6; 65°, 88.1; 70°, 109; 75°, 134; 80°, 164; 85°, 199; 90°, 239; 95°, 286; 100°, 339; 105°, 400; 110°, 470; 115°, 550; 120°, 640; 125°, 743; and 125.7°, 760. Using the vapour-pressure curve in the way suggested by Hillebrand (A., 1915, ii, 416), the value 13.9 is obtained for the entropy

of vaporisation divided by R at the temperature (70°) at which the concentration of the vapour is 0.00507 mol. per litre. Assuming that the vapour is normal, this would indicate slight, if any, association or abnormality in the liquid at this temperature.

J. F. S.

The Oxidation of Ethyl Alcohol by means of Potassium Permanganate.

WILLIAM LLOYD EVANS and JESSE E. DAY (*J. Amer. Chem. Soc.*, 1919, **41**, 1267—1285. Compare A., 1916, i, 362).—The series of experiments described in this communication are designed to elucidate the following points: (1) the nature of the products formed when ethyl alcohol is oxidised by neutral or alkaline permanganate at different temperatures; (2) the effect of changing the temperature and altering the initial concentration of alkali, and the combined effect of varying these factors; (3) the mechanism of the oxidation. The analytical methods are fully described, and a simple apparatus is illustrated in the text by means of which clear samples of the filtrate from the oxides of manganese can be obtained without exposure to the carbon dioxide of the atmosphere. In the experiments, just sufficient of a 9.21% solution of alcohol was added to 30 grams of 100% permanganate dissolved in 1000 c.c. of various solutions of potassium hydroxide to cause reduction.

The results are reproduced in a set of curves, as follows: (A) The weights of alcohol required to reduce a constant weight of permanganate at 25° , 50° , 75° , and 100° are plotted against the different concentrations of alkali, and the curves show that beyond a concentration of about 100 grams per litre, the proportion of potassium hydroxide is immaterial, whilst up to this point both increase of temperature and increased alkalinity accelerate the reduction. (B) The quantities of the oxidation products, acetic, oxalic, and carbonic acids, given by 0.1 gram-mol. of alcohol are plotted against concentrations of alkali for the four different temperatures. In neutral solutions the sole product is acetic acid, and in the experiments at 100° it is still only acetic acid as long as the concentration of alkali is less than 0.461 gram per litre. With the increase in the amount of potassium hydroxide, however, up to the maximum effect (100 grams per litre), the production of acetic acid diminishes and that of oxalic acid and carbon dioxide increases. (C) The quantities of the three oxidation products are separately plotted against alkali concentrations for the four temperatures. With increase of temperature, it appears that the yield of acetic acid falls, and the quantities of oxalic acid and carbon dioxide increase.

Another set of curves shows the connexion between the logarithms of the quantities of acetic acid produced and the logarithms of the initial concentrations of potassium hydroxide. These curves may be reproduced by the equation $y = B/x^a$, where y is the concentration of the acetic acid, x is the concentration of the alkali, a is the tangent of the line, and B is a constant, whence $\log y = \log B - a \log x$. From the values of B and a for the four

temperatures, it is possible to calculate the maximum concentration of alkali which will still permit of a theoretical yield of acetic acid. These are as follows:

Temperature.....	25°	50°	75°	100°
KOH, grams per litre...	2.55	1.19	0.655	0.460

That is, it is possible to obtain acetic acid only, no matter what the temperature, if the concentration of alkali is kept below these limits. On the other hand, if the tangents of the acetic acid log. curves (the above values of a) are plotted against temperature, a straight line is obtained which, if continued, meets the point at which $a=0$ on an axis of T corresponding with -25° ; this means that below this temperature the yield of acetic acid would be quantitative, no matter what the concentration of potassium hydroxide.

The mechanism of the formation of oxalic acid and carbon dioxide is discussed. The experiments support the views of other workers, namely, that the oxalic acid is not formed from acetic or formic acid, but from a derivative of acetaldehyde.

J. C. W.

The Temperature of Critical Solution of a Ternary Mixture as a Criterion of Purity of n -Butyl Alcohol. The Preparation of Pure n -Butyl Alcohol. KENNEDY JOSEPH PREVITÉ ORTON and DAVID CHARLES JONES (*T.*, 1919, **115**, 1194—1203).

The Preparation of $\alpha\beta$ -Dichloroethyl Ether. E. A. WILDMAN and HAROLD GRAY (*J. Amer. Chem. Soc.*, 1919, **41**, 1122—1123).—Dichloroethyl ether may be obtained by the direct chlorination of ethyl ether (Fritsch and Schumacher, *A.*, 1894, i, 485), but the operation is accompanied by two risks: (1) If the liquid is not well cooled at the outset, and the chlorine is admitted too rapidly, explosion may be caused by the inflammation of the ether vapour. This risk is lessened when the liquid is saturated with hydrogen chloride, and then the operation may be carried on rapidly. (2) Hydrogen chloride seems to form a super-saturated solution in ethyl ether, which may suddenly break out like a geyser; to obviate this, continuous, rapid agitation is necessary.

In order to get a pure product, b. p. $66-69^{\circ}/45$ mm., chlorination must be stopped when the density is 0.96. Starting with 800 grams of ethyl ether, this point is reached in about eighty-two hours, and the yield is about 375 grams.

J. C. W.

Action of Metallic Hydroxides and Oxides and Alkaline-earth Carbonates on Methyl Sulphates. J. GUYOT and L. J. SIMON (*Compt. rend.*, 1919, **169**, 534—537).—The behaviour of methyl sulphate in the presence of alkali hydroxides or alkaline earth oxides, hydroxides, or carbonates, depends to a large extent on the experimental conditions.

With potassium hydroxide in equimolecular proportions in methyl-alcoholic solution, methyl sulphate gives an almost quantitative yield of potassium methyl sulphate. A similar reaction occurs with calcium or barium hydroxide in the presence of a large excess of water. On the other hand, methyl sulphate may be distilled unchanged from barium or calcium oxide. With barium or calcium hydroxides in the absence of water, the action is $\text{Me}_2\text{SO}_4 + \text{M}(\text{OH})_2 = \text{MSO}_4 + \text{Me}_2\text{O} + \text{H}_2\text{O}$.

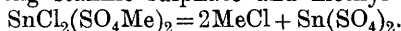
With cuprous, lead, mercuric, or silver oxides the action is, for example, $\text{Me}_2\text{SO}_4 + \text{Cu}_2\text{O} = \text{Cu}_2\text{SO}_4 + \text{Me}_2\text{O}$.

Methyl sulphate may be distilled unchanged from a small amount of an alkaline earth carbonate, but if kept at 140° for some time in the presence of the carbonate, it is decomposed according to the equation $\text{Me}_2\text{SO}_4 + \text{MCO}_3 = \text{MSO}_4 + \text{CO}_2 + \text{Me}_2\text{O}$, the reaction being slow.

W. G.

The Action of Stannic Chloride on Methyl Sulphate.

CH. BOULIN and L. J. SIMON (*Compt. rend.*, 1919, **169**, 618—620).—Stannic chloride acts on methyl sulphate in two stages, which may overlap, methyl chloride being, in each case, the gas liberated. If the action takes place at the ordinary temperature, it is represented by the equation $\text{SnCl}_4 + 2\text{Me}_2\text{SO}_4 = 2\text{MeCl} + \text{SnCl}_2(\text{SO}_4\text{Me})_2$, the methosulphate of stannyl chloride being obtained as a white, amorphous solid. At higher temperatures, this compound is decomposed, giving stannic sulphate and methyl chloride,



The use of an excess of methyl sulphate does not modify the sense of the complete reaction, but seems to favour the second stage.

The methosulphate of stannyl chloride is decomposed by aqueous potassium hydroxide, giving stannic hydroxide, potassium chloride, and potassium methyl sulphate.

W. G.

Methionic [Methanedisulphonic] Acid and its Applications in Syntheses. G. SCHROETER [with G. KOCH, G. HERZBERG, TH. MARIAM, W. SONDAG, C. FRESSENIUS, W. ROTHMANN, A. GLUSCHKE, R. VON BUTLAR-BRANDENFELS, W. DORN, DIESSELHORST, E. KINDERMANN, EMMY SCHROETER, and O. CARLÉ] (*Annalen*, 1919, **418**, 161—257).—Portions of this paper have been published during the last twenty-two years.

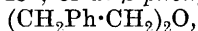
A description is given of the preparation of methanedisulphonic acid from acetylene (350—400 grams) and fuming sulphuric acid (65—70% SO_3) (about 6 kilos.) through the barium salt (700 grams of the salt from 1 kilo. of acid). The presence of phenol among the by-products, recorded by Berthelot in 1869, has been confirmed, and an explanation of its formation is suggested.

The reactions of methanedisulphonic acid have been thoroughly studied in the expectation of finding for it synthetic uses similar to those of malonic acid.

Improvements in the method of preparing methyl methane-disulphonate from the silver salt and methyl iodide (Schroeter and Herzberg, A., 1905, i, 851) are described; the ethyl ester has

been obtained in flattened needles, m. p. 28—29°. An attempt to prepare the benzyl ester from the silver salt and benzyl chloride in boiling benzene resulted in the formation of hydrogen chloride and diphenylmethane, the silver salt acting (so also does silver sulphate) simply as a catalyst.

Alkyl methanedisulphonates can also be prepared from alcohols and methanedisulphonyl chloride, but the method is not a suitable one, because, unless the violence of the reaction is moderated by the presence of a suitable diluent (ethyl ether), the resulting esters decompose into methanedisulphonic acid and ethers. The tendency of alkyl methanedisulphonates to decompose into methanedisulphonic acid and ethers (Schroeter and Sondag, A., 1908, i, 497) has been utilised in the preparation of heptyl ether, b. p. 126—127°/8 mm., D^{20}_D 0.8056, from heptyl alcohol and methanedisulphonyl chloride at 145°, of *di-β-phenylethyl ether*,



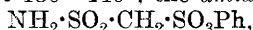
b. p. 175—176°/8 mm., D^{15}_D 1.0178 (a little styrene is also formed), from *β*-phenylethyl alcohol, and of *cyclohexene* from *cyclohexanol* in a similar manner. Aryl methanedisulphonates, on the contrary, are very stable compounds, and must be heated with a concentrated solution (50%) of alkali hydroxide to decompose them into phenols and methanedisulphonic acid. In consequence of the acidity of the methylene group between the two $\cdot\text{SO}_3\text{Ar}$ groups, the aryl esters dissolve in concentrated aqueous ammonia and in dilute solutions of alkali hydroxides. They resemble the phenols in their antiseptic and bactericidal actions. *Phenyl methanedisulphonate (methionol)*, $\text{CH}_2(\text{SO}_3\text{Ph})_2$, prepared from methanedisulphonyl chloride and phenol (4 mols.) in boiling toluene, forms colourless needles, m. p. 82°; the *sodio*- and *potassio*-derivatives, $\text{CHNa}(\text{or K})(\text{SO}_3\text{Ph})_2$, are crystalline, and the *argento*-derivative is a colourless powder. The *dibromo*-derivative, $\text{CBr}_2(\text{SO}_3\text{Ph})_2$, forms colourless crystals, m. p. 58—59°. The *o*-, *m*-, and *p*-*tolyl* esters, $\text{CH}_2(\text{SO}_2\cdot\text{O}\cdot\text{C}_6\text{H}_7)_2$, form crystals, m. p. 84°, 56°, and 84° respectively, whilst the *guaiacol* and *catechol* esters have m. p. 90° and 190° respectively.

Methanedisulphonyl chloride (Schroeter and Sondag, *loc. cit.*) has been obtained in two modifications. The liquid form usually obtained, m. p. 8°, D^{15}_D 1.831, is converted under conditions which have not yet been definitely ascertained into a second modification, long needles or prisms, m. p. 36—37°; the liquid form is converted into the solid by inoculation with the latter, and the solid form is converted into the liquid by warming above the m. p.

Methanedisulphonyl chloride reacts abnormally with dry ammonia in chloroform solution and with diethylamine in ethereal solution, the products in both cases being, not the expected amides, but mixtures of substances the nature of which has not yet been ascertained. The reaction with aniline (4 mols.) in chloroform or benzene solution, however, is normal (Schroeter and Herzberg, *loc. cit.*). *Methanedisulphonacetanilide*, $\text{CH}_2(\text{SO}_2\cdot\text{NAcPh})_2$, m. p. 196—197°, *methanedisulphonbenzanilide*, m. p. 204—205°, *methanedisulphonmethylanilide*, colourless needles, m. p. 141.5—142.5°

methanedisulphonethylanilide, m. p. 112—114°, *methanedisulphonanilidoethylanilide*, $\text{CH}_2(\text{SO}_2\cdot\text{NHPh})(\text{SO}_2\cdot\text{NEtPh})$, m. p. 168°, *methanedisulphonphenetidide*, $\text{CH}_2(\text{SO}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OEt})_2$, m. p. 221°, and its *methyl*-, m. p. 132—133°, *ethyl*-, m. p. 141—142°, and *aceto-phenetidides*, m. p. 155°, *methanedisulphon-p-nitroanilide*, yellow needles, carbonising above 240°, and *methanedisulphondiphenylamide*, $\text{CH}_2(\text{SO}_2\cdot\text{NPh}_2)_2$, m. p. 228°, have been prepared. The preceding primary anilides are moderately strong acids forming sodium and barium derivatives and decomposing carbonates, but anilides which do not contain the NH-group are devoid of acid character, being insoluble in aqueous alkali hydroxide solution.

When a solution of phenyl methanedisulphonate in benzene saturated with ammonia is treated with an equal quantity of phenyl methanedisulphonate and the mixture is heated in a sealed tube for three hours at 130—140°, the *amide ester*,



crystals, m. p. 16°, is obtained; the same substance is also obtained by heating phenyl methanedisulphonate and carbamide in a sealed tube at 140—160°. When a solution of phenyl methanedisulphonate in benzene supersaturated with ammonia is heated in a sealed tube at 140—145°, *methanedisulphonamide*, $\text{CH}_2(\text{SO}_2\cdot\text{NH}_2)_2$, leaflets, m. p. 233°, is obtained; it forms *sodium* and *barium* derivatives and a *monobenzoyl* derivative, leaflets, m. p. 216°. *Methanedisulphonethylanilide*, $\text{CH}_2(\text{SO}_2\cdot\text{NHEt})_2$, similarly prepared by means of a benzene solution of ethylamine, forms leaflets, m. p. 143—145°.

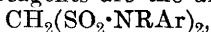
Methanedisulphonyl chloride reacts normally with esters of amino-acids in cold ethereal or chloroform solution. Thus, ethyl glycine and ethyl phenylglycine yield, respectively, *ethyl methanedisulphonaminoacetate*, $\text{CH}_2(\text{SO}_2\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et})_2$, colourless needles, m. p. 113·5°, and *ethyl methanedisulphonanilinoacetate*, $\text{CH}_2(\text{SO}_2\cdot\text{NPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et})_2$, colourless needles, m. p. 109—111°; the former is soluble in dilute alkali hydroxides and in aqueous ammonia, whilst the latter dissolves sodium or potassium with the evolution of hydrogen, and is hydrolysed by aqueous-alcoholic sodium hydroxide, yielding *methanedisulphonanilinoacetic acid*, $\text{CH}_2(\text{SO}_2\cdot\text{NPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$, crystals with $2\text{H}_2\text{O}$, m. p. 110—112° (anhydrous).

Methanedisulphonphenylhydrazide, $\text{CH}_2(\text{SO}_2\cdot\text{NH}\cdot\text{NHPh})_2$, colourless needles, m. p. 118—119° (decomp.), and *methanedisulphonbenzoylhydrazide*, $\text{CH}_2(\text{SO}_2\cdot\text{NH}\cdot\text{NHBz})_2$, needles, m. p. 204—205° (decomp.), are prepared from methanedisulphonyl chloride and phenyl- and benzoyl-hydrazine, respectively, in ethereal or chloroform solution; the latter is soluble in aqueous alkali hydroxide.

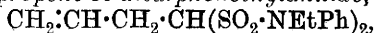
By introducing alkyl, aryl, and acyl groups in the methylene group, syntheses have been effected both with the esters and the amide derivatives of methanedisulphonic acid, but the replacement of the methylene hydrogen atoms by metals, and consequently also the course of the synthesis, depend on the nature of the

radicles attached to the SO_2 groups. The methyl and ethyl esters in ethereal or benzene solution react with the alkali metals, with the evolution of hydrogen, but the reaction becomes so slow before one atomic proportion of the metal has been added that syntheses attempted by this means follow a tedious and uncertain course; however, *ethane- $\alpha\alpha$ -disulphonic acid* and *propane- $\alpha\alpha$ -disulphonic acid* in the form of their *barium* salts have been obtained by the action of methyl and ethyl iodides, respectively, on a benzene solution of the methyl or ethyl methanedisulphonate to which potassium had been previously added. Aryl esters of methanedisulphonic acid form in aqueous solution stable salts with alkali hydroxides and with ammonia, but these salts, from some undetermined cause, are little suited for synthetic purposes in aqueous or alcoholic solution or suspension. When, however, the aryl esters are treated in an indifferent solvent with sodium, and the resulting solution or suspension is treated with alkyl haloid, methyl sulphate, or benzoyl chloride, reaction proceeds smoothly. *Phenyl ethane- $\alpha\alpha$ -disulphonate*, $\text{CHMe}(\text{SO}_2\text{Ph})_2$, *phenyl propane- $\alpha\alpha$ -disulphonate*, *phenyl propane- $\beta\beta$ -disulphonate*, crystals, m. p. 96—97°, and *phenyl butane- $\beta\beta$ -disulphonate*, an oil, have been thus prepared; also *p-tolyl ethane- $\alpha\alpha$ -disulphonate*, crystals, m. p. 57—60°, and *p-tolyl propane- $\beta\beta$ -disulphonate*, crystals, m. p. 88—91°, have been obtained, whilst the corresponding *o*-tolyl and *m*-tolyl esters are oily liquids.

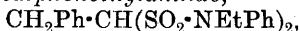
Numerous syntheses can be effected by means of the amide derivatives of methanedisulphonic acid. Any such derivative containing the NH group is inadmissible, however, because such substances form metallic derivatives containing the NNa group, and these lead to the production of *N*-substituted derivatives. The most efficient synthetic reagents are the alkylanilides,



particularly the very easily obtainable methanedisulphonethyl-anilide. These substances in warm benzene solution are treated with sodium or potassium, and the product is treated with an alkyl or acyl haloid. By these means, the CH_2 group of the methanedisulphonalkylanilides can be converted into CHMe , CHEt , $\text{CH} \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2$, $\text{CH} \cdot \text{CH}_2 \cdot \text{Ph}$, and $\text{CH} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ (*p*), but alkyl haloids of greater complexity react very slowly. Further, the remaining hydrogen atom of the preceding groups can be replaced by a methyl group, giving CMe_3 , CMeEt , etc., but not by an ethyl, allyl, or other radicle. Analogously to the preceding, the sodium derivatives, $\text{CHNa}(\text{SO}_2 \cdot \text{NRAr})_2$, react with the halogens, yielding derivatives containing the group CHCl , CHBr , or CHI ; from these, a dichloro-derivative, $\text{CCl}_2(\text{SO}_2 \cdot \text{NRAr})_2$, can be obtained, but not a dibromo- or di-iodo-derivative. *Ethane- $\alpha\alpha$ -disulphonethyl-anilide*, $\text{CHMe}(\text{SO}_2 \cdot \text{NEtPh})_2$, prisms, m. p. 150°, *ethane- $\alpha\alpha$ -disulphonethylphenetide*, crystals, m. p. 95—96·5°, *propane- $\alpha\alpha$ -disulphonethyl-anilide*, prisms, m. p. 128—129°, and the *-phenetide*, $\text{CHEt}(\text{SO}_2 \cdot \text{NEt} \cdot \text{C}_6\text{H}_4 \cdot \text{OEt})_2$, needles, m. p. 93·5—94·5°, Δ^1 -*propene- $\delta\delta$ -disulphonethyl-anilide*,



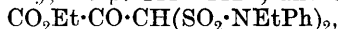
prisms, m. p. 120—121° (*dibromide*, needles, m. p. 103—106°), *β-phenylethane-αα-disulphonethylanilide*,



prisms, m. p. 104—106°, *β-p-nitrophenylethane-αα-disulphonethylanilide*, pale yellow, crystalline powder, m. p. 100—105°, *propane-ββ-disulphonethylanilide*, crystals, m. p. 130—132°, and the *-phenetidine*, m. p. 109°, *butane-ββ-disulphonethylanilide*, crystals, m. p. 114—116°, *Δ^α-pentene-δδ-disulphonethylanilide*, m. p. 107° (*dibromide*, leaflets, m. p. 100—102°), and *α-phenylpropane-ββ-disulphonethylanilide*, m. p. 96·5—97°, are described.

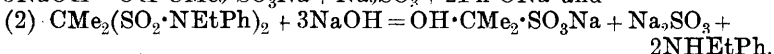
Phenyl benzoylmethanedisulphonate, $\text{CHBz}(\text{SO}_3\text{Ph})_2$, crystals, m. p. 96°, and the corresponding *p-tolyl* ester, m. p. 91°, and *m-tolyl* ester, m. p. 102°, have been prepared.

The following acyl derivatives of methanedisulphonethylanilide are described: *formyl*, $\text{CHO}\cdot\text{CH}(\text{SO}_2\cdot\text{NEtPh})_2$, needles, m. p. 113—114°; *acetyl*, rhombic plates, m. p. 143—144°; *propionyl*, needles, m. p. 129—130°; *benzoyl*, m. p. 118—119°; *o-nitrobenzoyl*, prisms, m. p. 148—149°; *o-acetoxybenzoyl*, m. p. 152—153°; *carbethoxy*, m. p. 111—112°; and *ethoxalyl*,



plates, m. p. 103—105°. *Chloromethanedisulphonethylanilide*, $\text{CHCl}(\text{SO}_2\cdot\text{NEtPh})_2$, needles, m. p. 97—98°, the *bromo-derivative*, needles, m. p. 167—168°, the *iodo-derivative*, needles, decomp. 150—170°, and *dichloro-derivative*, m. p. 109—110°, are described.

Unlike malonic acid, methanedisulphonic acid is very stable towards mineral acids, so much so that the Carius method is inapplicable to the estimation of the sulphur. The aryl esters and anilides of the dialkylated acids, $\text{C}(\text{Alk.})_2(\text{SO}_3\text{H})_2$, are resistant to acid hydrolysis, but are smoothly decomposed by alcoholic alkalis under pressure in the sense of the equations: (1) $\text{CMe}_2(\text{SO}_3\text{Ph})_2 + 5\text{NaOH} = \text{OH}\cdot\text{CMe}_2\cdot\text{SO}_3\text{Na} + \text{Na}_2\text{SO}_3 + 2\text{Ph}\cdot\text{ONa}$ and



Sodium *β*-hydroxypropane-*β*-sulphonate thus obtained is not identical with the additive compound of acetone and sodium hydrogen sulphite.

Acyl derivatives of aryl esters or secondary anilides of methanedisulphonic acid are extraordinarily stable towards alkalis; the latter class of compound is decomposed by heating with mineral acids in the sense of the equation $\text{CHBz}(\text{SO}_2\cdot\text{NEtPh})_2 + 3\text{H}_2\text{O} = \text{CH}_2\text{Bz}\cdot\text{SO}_3\text{H} + \text{H}_2\text{SO}_4 + 2\text{NHetPh}$. C. S.

Dehydration of Formic Acid Solutions. D. C. JONES (*J. Soc. Chem. Ind.*, 1919, **38**, 362—363r).—It is shown that, in spite of previous statements to the contrary, phosphoric oxide can be used satisfactorily for the dehydration of concentrated solutions of formic acid. The conditions to be observed are that the calculated quantity of phosphoric oxide necessary to combine with the water present in the formic acid be added gradually, the mixture being well cooled and shaken during the addition. The formic acid is then distilled under 15—18 mm. pressure, and can

readily be obtained up to 99·5% strength. When excess of phosphoric oxide is used, considerable decomposition of the formic acid occurs.

The concentration of dilute solutions of formic acid is limited by the formation of a constant boiling mixture containing 77% of acid by weight and boiling at 107·1°. The composition of the constant boiling mixture is found to vary to a considerable degree with the pressure, decreasing in formic acid content with diminishing pressure, until at 43 mm. it contains 60·9% of formic acid, the boiling point being 38°. It is therefore possible to obtain concentrated from dilute formic acid by concentrating up to the constant boiling mixture at atmospheric pressure, and then continuing the distillation at low pressure, a separation into very concentrated formic acid and the more dilute constant boiling mixture being obtained.

E. H. R.

Preparation of Anhydrides and Chlorides of Organic Acids.

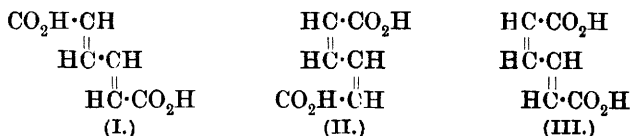
THOMAS HAROLD DURRANS and A. BOAKE, ROBERTS & CO., LTD. (Brit. Pat., 131379; addition to Brit. Pat., 128282).—Organic acid anhydrides or chlorides other than acetic anhydride or chloride may be produced by the action of chlorine on a mixture of phosphorus, preferably red phosphorus, and the alkali or alkaline earth salts of the organic acid, at temperatures preferably below 50°, and in proportions falling within those represented by the following pairs of equations for the anhydrides and chlorides respectively: $6R\cdot CO_2Na + P + 3Cl = 3(R\cdot CO)_2O + Na_3PO_3 + 3NaCl$ and $8R\cdot CO_2Na + P + 5Cl = 4(R\cdot CO)_2O + Na_3PO_4 + 5NaCl$, $3R\cdot CO_2Na + P + 3Cl = 3R\cdot COCl + Na_3PO_3$ and $4R\cdot CO_2Na + P + 5Cl = 4R\cdot COCl + Na_3PO_4$.

G. F. M.

The Action of Grignard Reagents on the Esters of certain Dicarboxylic Acids. HARRY HEPWORTH (T., 1919, 115, 1203—1210).

Oxidation of Muconic Acid. Synthesis of Mucic Acid.

ROBERT BEHREND and GEORGE HEYER (*Annalen*, 1919, 418, 294—316).—Of the three configurative formulæ possible for muconic acid, formula I is the most probable, since the only tar-



taric acid produced by oxidation with permanganate is *r*-tartaric acid; formic, carbonic, oxalic, mucic, and other unidentified acids are also formed, but the absence of *i*-tartaric acid is definitely ascertained.

Mucic acid is obtained in yields up to 36·5% of the theoretical by oxidising a neutral solution of sodium muconate with sodium chlorate in the presence of a little osmium tetroxide and a few

*y**

drops of acetic acid (compare Hofmann, Ehrhart, and Schneider, A., 1913, ii, 609), *r*-idosaccharic acid being also formed in about 2% of the theoretical yield. The latter acid forms a characteristic copper salt, $C_6H_8O_8Cu \cdot 2H_2O$, microscopic prisms which become deep blue by prolonged heating at 120° , and a *phenylhydrazide*, $C_{18}H_{22}O_6N_4$, faintly yellowish-white, crystalline powder, m. p. $217-218^\circ$ (decomp.). C. S.

Reactions between Potassium Sulphate and Tartaric Acid under Various Conditions. Behaviour of Potassium Hydrogen Sulphate with Alcohol. ARTURO BORNTAEGER (*Annali Chim. Appl.*, 1919, 12, 1-23).—The readiness with which the system ($K_2SO_4 + C_4H_6O_6$) is converted into the system ($KHSO_4 + C_4H_5KO_6$) when evaporated with alcohol was shown by Bussy and Buignet (*J. Pharm. Chim.*, 1865, [v], 2, 8). When aqueous solutions containing equivalent quantities of potassium hydrogen sulphate and potassium hydrogen tartrate are evaporated, potassium sulphate and tartaric acid are first formed. On continuing the evaporation, potassium hydrogen tartrate is deposited, and this subsequently reacts with the potassium hydrogen sulphate in solution to form potassium sulphate and tartaric acid. Hence the two systems ($K_2SO_4 + C_4H_6O_6$) and ($KHSO_4 + C_4H_5O_6K$) appears to behave in an identical manner under these conditions. When the evaporation is continued to the end, a dry mixture of potassium sulphate and tartaric acid is obtained, whereas in presence of free sulphuric acid the residue would be moist. Absolutely anhydrous alcohol has no influence on potassium hydrogen sulphate, but alcohol containing a little water decomposes it slowly and partly into the normal sulphate and free sulphuric acid. On treating a dry mixture in equimolecular proportions of potassium sulphate and tartaric acid with ether or absolute alcohol, only the tartaric acid is extracted, but in presence of alcohol containing a little water, a partial reaction takes place, with the formation of potassium hydrogen tartrate and potassium hydrogen sulphate, and the latter is subsequently partly decomposed into the normal sulphate and free sulphuric acid. Similar reactions are observed when solutions of the two substances in equimolecular proportions are evaporated prior to the treatment with ether, absolute alcohol, or alcohol containing a little water. [See also *J. Soc. Chem. Ind.*, 1919, 839A.] C. A. M.

Crystallography of the Compound of Nickel Dichromate and Ethylenediamine, $NiCr_2O_7 \cdot 3C_2H_4(NH_2)_2$. GIUSEPPINA CHIAVARINO (*Riv. min. crist. Ital.*, 1917, 48, 82-85).—This salt is monoclinic; complete crystallographic data are given.

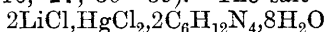
CHEMICAL ABSTRACTS.

Crystallography of the Compounds of Nickel and Magnesium Tetrathionate Octahydrates with Hexamethylenetetramine. C. PERRIER (*Riv. min. crist. Ital.*, 1916, 47, 22-30).—The salts of the formula $RS_4O_6 \cdot 2C_6H_{12}N_4 \cdot 8H_2O$,

where R=Mg or Ni, are monoclinic; complete crystallographic data are given. The isomorphism of magnesium and nickel in other compounds is discussed, and the closeness of their molecular volumes is pointed out.

CHEMICAL ABSTRACTS.

Crystallography of Compounds of Lithium Mercuric Haloids with Hexamethylenetetramine. E. QUERCIGH (*Riv. min. crist. Ital.*, 1916, **47**, 30—39).—The salt



is monoclinic, the corresponding bromide triclinic, and the iodide rhombic. Full crystallographic data are given.

CHEMICAL ABSTRACTS.

The Melting Points of the Substituted Amides of the Normal Fatty Acids. PHILIP WILFRED ROBERTSON (T., 1919, **115**, 1210—1223).

Action of Alkaline Solutions of Bromine on Acid Amides. HANS ODENWALD (*Annalen*, 1919, **418**, 316—341).—In the method previously described (Behrend and Odenwald, this vol., i, 70) for the preparation of acetylmethylcarbamide, the yield falls from 75% to zero in the presence of an excess (15—20%) of alkali over the amount (1 mol.) required to react with the acetamide (1 mol.) and bromine (0.55 mol.). The cause of this has now been investigated. In a series of experiments, acetamide (1 mol.) was dissolved in bromine (0.5—2.0 mols.), and the solution was treated with a quantity of 18.7% potassium hydroxide solution (1.2—4.8 mols.) 20% in excess of the amount required to combine with the bromine. Carbon dioxide, ammonia, and methylamine were detected in all experiments; the amounts of these and of unchanged acetamide, in the experiments with less than 1.5 mols. of bromine, account for 0.47—0.49 mol. of acetamide. With 1.5 mols. of bromine, acetylmethylcarbamide (0.078 mol.) was detected, but not acetamide, and in the experiment with 2 mols. of bromine neither acetamide nor acetylmethylcarbamide could be detected, and the amount of carbon dioxide formed corresponded with only 0.3 mol. of acetamide. In all experiments, the balance of the acetamide was converted into products which could not be identified; the products were unsuccessfully examined for the presence of acetonitrile, methyl alcohol, hydrogen cyanide, s-dimethylcarbamide, and methylcarbamide, but very small quantities of dibromomethylamine and of nitrogen (about 0.03 mol.) were detected. The author is of opinion that the methylcarbamide in alkaline solution reacts with acetamide either not at all or very much more slowly than in acid solution; instead of forming acetylmethylcarbamide, it decomposes into carbon dioxide and methylamine, and the latter reacts more rapidly than acetamide with the hypobromite.

With the hope of obtaining less volatile products of reaction, the behaviour of an alkaline solution of bromine with isovaleramide has been examined. In an experiment with isovaleramide

(0.5 mol.), bromine (0.25 mol.), and 10% potassium hydroxide solution (0.6 mol.), the products were carbon dioxide (0.23 mol.), dibromo*isobutylamine* (0.09 mol.), ammonia and *isobutylamine* (0.02 mol.); these and unchanged *isovaleramide* (0.32 mol.) account for the whole of the amide. The reaction proceeds according to the equation $\text{C}_4\text{H}_9\cdot\text{CO}\cdot\text{NH}_2 + \text{Br}_2 + 2\text{KOH} = \text{C}_4\text{H}_9\cdot\text{NH}_2 + \text{CO}_2 + 2\text{KBr} + \text{H}_2\text{O}$, but the author has been unable to discover what is the fate of the *isobutylamine*.

It is possible that a loss of acetamide occurs in the first experiments during the evaporation of solutions. One gram of different amides has been evaporated to dryness with 20 c.c. of water, heated on the water-bath for half an hour, and again evaporated with 20 c.c. of water; the losses were, with acetamide 0.95 gram, with propionamide 0.36 gram, with *isobutyramide* 0.10 gram, and with *isovaleramide* nil.

It is quite immaterial in what order acetamide (1 mol.), *isovaleramide* (1 mol.), bromine (1 mol.), and aqueous potassium hydroxide (2 mols.) are mixed together; the products of the reaction are always the same, namely, about equal quantities (molecular) of *isovalerylisobutylcarbamide* and *acetylisobutylcarbamide*, together with a small quantity of *acetylmethylcarbamide*; it is remarkable that the fourth possible product, *isovalerylmethylcarbamide*, could not be detected. Analogous results are obtained with acetamide and propionamide, and with acetamide and *isobutyramide*.

Acetylisobutylcarbamide, $\text{C}_7\text{H}_{14}\text{O}_2\text{N}_2$, forms long, six-sided leaflets, m. p. 109—114°, and *acetylisopropylcarbamide*, hexagonal crystals, m. p. 68—72°, which become superficially oily after long keeping. C. S.

The Constitution of Carbamides. X. The Behaviour of Urea and of Thiourea towards Diazomethane and Diazoethane respectively. The Oxidation of Thiourea by Potassium Permanganate. EMIL ALPHONSE WERNER (T., 1919, 115, 1168—1174).

Some Cases of Solubility Influence. I. Compounds of Thiosinamine [Allylthiocarbamide] Existing in Aqueous Solution. G. BARGELLINI (*Gazzetta*, 1919, 49, i, 175—191).—Cryoscopic investigation of solutions containing thiocarbamide or allylthiocarbamide, together with either sodium salicylate or resorcinol or antipyrine, leads to anomalous results which are explainable on the assumption that compounds between the different pairs of solutes are formed in solution. None of these compounds has been separated in the solid condition. T. H. P.

The Rotatory Powers of the Amides of Several α -Hydroxyacids of the Sugar Group. C. S. HUDSON and SHIGERU KOMATSU (*J. Amer. Chem. Soc.*, 1919, 41, 1141—1147).—The generalisations announced in an earlier paper, based largely on Weerman's work (A., 1918, i, 292), have been amplified and extended by further

and more trustworthy data. The material examined makes it possible to calculate the molecular rotation due to each active carbon atom in a number of series by the method already employed in the case of certain phenylhydrazides (A., 1917, i, 318). The following table gives the values as far as it is possible to determine them, the sign of the rotation being for the isomeride which has the hydroxyl group attached to the particular carbon atom placed to the right of the formula, written vertically, with the amide group at the top.

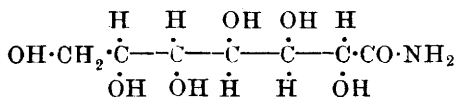
Carbon.	4-C series diamide.	Pentonic amides.	Hexonic amides.	Heptonic amides.	Hexaric diamides.
α	+7880	+4450	+4725	+4585	+3925
β	—	-2315	-1465	-1960	-1385
γ	—	+575	+95	?	—
δ	—	—	-205	-420	—

The values for the β - and γ -carbon atoms in the series of pentonic amides are probably untrustworthy, as they depend on a value of the rotation of *d*-xylonamide which is doubtful.

It is interesting to note how the sign of the rotation alternates from carbon to carbon, and how much the rotation of the whole molecule depends on the configuration about the α - and β -carbon atoms. The table also illustrates the principle of optical superposition in the sugar group.

The amides prepared by the authors themselves, usually by the action of ammonia on the lactones, are as follows, the values of $[\alpha]_D^{20}$ being for aqueous solutions: *d*-galactonamide, m. p. 172—172.5°, $[\alpha]_D^{20} + 30.2^\circ$; *d*-gluconamide, m. p. 143—144°, $[\alpha]_D^{20} + 31.2^\circ$; *d*-gulonamide, m. p. 122—123°, $[\alpha]_D^{20} + 15.2^\circ$; *d*-mannonamide, m. p. 172—173°, $[\alpha]_D^{20} - 17.3^\circ$; α -*d*-glucoheptonamide, m. p. 134.5°, $[\alpha]_D^{20} + 10.6^\circ$; β -*d*-glucoheptonamide, m. p. 158°, $[\alpha]_D^{20} - 30.2^\circ$; α -*d*-galaheptonamide, m. p. 206°, $[\alpha]_D^{20} + 14.3^\circ$; *l*-arabonamide, m. p. 135—136°, $[\alpha]_D^{20} + 37.5^\circ$; *l*-ribonamide, m. p. 137—138°, $[\alpha]_D^{20} - 16.4^\circ$; *d*-mannosaccharodiamide, m. p. 188—189.5° (decomp.), $[\alpha]_D^{20} - 24.5^\circ$; *d*-saccharodiamide, m. p. 172—173°, $[\alpha]_D^{20} + 13.3^\circ$. J. C. W.

The Amide of α -*d*-Mannoheptonic Acid. C. S. HUDSON and K. P. MONROE (*J. Amer. Chem. Soc.*, 1919, **41**, 1140—1141).—This amide was first obtained by Fischer by the action of hydrogen cyanide on *d*-mannose, but it is not easy to purify it if made in this way. A better method is the action of ammonia on a solution of α -*d*-mannoheptonolactone in 50% alcohol. α -*d*-Mannoheptonamide (annexed formula) has m. p. 193—194° and $[\alpha]_D^{20} + 28.0^\circ$, the molecular rotation being almost the same as that of *d*-galacton-



amide and *l*-arabonamide, in which the configuration of the molecule with regard to the α -, β -, and γ -carbon atoms is the same.

J. C. W.

Preparation of Cyanogen Chloride. W. L. JENNINGS and W. B. SCOTT (*J. Amer. Chem. Soc.*, 1919, **41**, 1241—1248).—The authors review the history of cyanogen chloride, and report that the most suitable reaction for its preparation is that of chlorine on an alkali cyanide. Water is necessary in this reaction, but its amount must be restricted, otherwise too much heat is developed and some of the product is polymerised. The best procedure is as follows. Finely powdered sodium cyanide is mixed with 2% of its weight of water and just sufficient carbon tetrachloride to prevent the mass from becoming pasty. The mixture is cooled to -5° and submitted to the action of a current of well-washed chlorine, so regulated that the temperature is maintained at about -3° . The flask is connected with a calcium chloride tube and then a U-tube immersed in a freezing mixture, and when absorption is complete, as indicated by a bubbler at the final exit, the temperature is allowed to rise to 10° , and finally to 28° , so as to distil the cyanogen chloride. The crude product is usually of a yellow colour through dissolved chlorine, but this is removed by freezing or by leaving the liquid over mercury in a sealed tube. The yield is almost quantitative, and there are no risks of explosion.

Pure cyanogen chloride is a colourless liquid, b. p. $13^{\circ}/748$ mm., m. p. -5° to -6° , and does not polymerise. The presence of traces of hydrogen chloride, however, induces polymerisation, and if suspected should be counteracted by treatment with lime.

J. C. W.

Preparation of Cyanogen Chloride by Held's Method. CH. MAUGUIN and L. J. SIMON (*Compt. rend.*, 1919, **169**, 383—386).—Held's method for preparing cyanogen chloride from potassium cyanide and chlorine (A., 1898, i, 547) gives good results only if the proportion of zinc sulphate added is that required by the equation $4\text{KCN} + \text{ZnSO}_4 = \text{Zn}(\text{CN})_2 + 2\text{KCN} + \text{K}_2\text{SO}_4$, a yield of 80% being then obtained. Methods for controlling the purity of the product are described.

T. H. P.

Compounds of Univalent Nickel. II. I. BELLUCCI (*Gazzetta*, 1919, **49**, ii, 70—81. Compare A., 1914, i, 260; also Tschugaev and Chlopin, A., 1914, ii, 660).—The aqueous solution of red potassium nickelocyanide, $\text{K}_2\text{Ni}(\text{CN})_3$, prepared by gradual addition of alkali metal amalgam to the aqueous solution of the yellow nickelocyanide, $\text{K}_2\text{Ni}(\text{CN})_4$, in an atmosphere of hydrogen, readily assumes the original yellow colour, oxidation being effected either by atmospheric oxygen, or by aqueous oxygen with liberation of the hydrogen, or by an oxidising agent such as hydrogen peroxide. The red solution may be preserved from appreciable oxidation for some days by employing boiled water in its preparation and by adding concentrated potassium hydroxide solution to the liquid and covering the latter with a layer of light petroleum.

Oxidation of the red nickelocyanide by means of hydrogen peroxide in absence of alkali cyanide takes place according to the

equation, $4K_2Ni(CN)_3 + 2H_2O_2 = 3K_2Ni(CN)_4 + Ni(OH)_2 + 2KOH$. Further, when an aqueous solution of the pure, red nickelocyanide is boiled for some time in a reflux apparatus in a stream of hydrogen, metallic nickel is precipitated, and the yellow nickelocyanide remains in the solution, the proportions of the total nickel in precipitate and solution being very nearly 1:3 (actually 1:3.16): $4K_2Ni(CN)_3 + 2H_2O = 3K_2Ni(CN)_4 + Ni + 2KOH + H_2$; the same reaction occurs, only far more slowly, at the ordinary temperature. Such separation of metallic nickel from a compound of univalent nickel may be represented by the scheme, $2Ni' \rightarrow Ni'' + Ni$, and is analogous to the separation of copper from a cuprous salt with formation of a cupric salt, $2Cu' \rightarrow Cu'' + Cu$.

T. H. P.

Production of Aromatic Nitro-compounds. FERDINAND GROS & BOUCHARDY and LUCIEN JEAN JOSEPH PERRUCHE (Brit. Pat., 131982).—Aromatic nitro-compounds are prepared by passing oxygen, air, or ozonised air, preferably under pressure, into a mixture of the substance to be nitrated with liquid nitrogen peroxide and traces of water, the temperature being maintained at 0–20°. Nitric acid is first produced according to the equation $N_2O_4 + H_2O + O = 2HNO_3$, and instantly reacts with the aromatic compound, regenerating water, and the cycle of operations is repeated until the reaction mixture contains only the nitro-compound, nitric acid, and the excess of nitrogen peroxide used; the last is recovered by distillation or by a current of hot air. The nitro-compound may then be isolated after neutralising the nitric acid, or it may be further nitrated by treating the residual mixture with sulphuric acid. If necessary, the violence of the nitration may be moderated by adding to the reaction mixture an inert diluent, such as carbon tetrachloride, before admitting the oxygen.

G. F. M.

Preparation of *N*-Monoalkyl Derivatives of certain Aromatic Compounds. ARTHUR LAPWORTH and LEVINSTEIN, LTD. (Eng. Pat., 132555).—Benzylidene derivatives of *p*-substituted monoamines or of other monoamines of the benzene and naphthalene series substituted by indifferent groups in the nucleus, which either as amines or as alkylamines do not react with benzaldehyde in the presence of acids to form amino-derivatives of triarylmethanes, are treated in the absence of alkali with alkyl sulphates or alkyl esters of benzenesulphonic acid. The products are hydrolysed and the *N*-monoalkylarylamine is separated from the mixture. Examples of the process are described in relation to the benzylidene derivatives of *p*-aminophenol, *p*-toluidine, and 1-bromo-2-naphthylamine. The benzylidene compound is dissolved in boiling benzene, the pure alkylating agent, such as methyl sulphate, is added, and the mixture boiled for some hours. The product is hydrolysed by the addition of hydrochloric acid and a little water, the benzaldehyde and benzene are removed by distillation with steam, the *N*-alkylated base is liberated from the residue and

separated from the other products in any suitable manner, for example, by conversion into the nitroso-compound. J. F. B.

Preparation of Diphenylamine. HOMER ROGERS and E. J. DU PONT DE NEMOURS & Co. (U.S. Pat. 1314538).—The condensation of aniline to diphenylamine is effected by heating the aniline in the presence of water and a catalyst consisting of a substance containing bromine. J. F. B.

β -Naphthylmethylamine. GILBERT T. MORGAN and FREDERICK PAGE EVANS (T., 1919, 115, 1140—1145).

The Oxidation of Phenol Derivatives. CYRIL NORMAN HINSHELWOOD (T., 1919, 115, 1180—1188).

Oxidation of Phenols by Gaseous Oxygen and the Catalytic Effect of Metals. F. W. SKIRROW (*Canadian Chem. J.*, 1919, 3, 292—294).—The oxidation which takes place when *o*-cresol or a solution of cresol in benzene is brought into contact with air or oxygen in the presence of copper was measured by connecting the tube containing the reacting substances with a mercury manometer and recording the rate of absorption by the fall in pressure. It was found that there was an initial period during which there was little, if any, absorption. In a blank experiment in which the air in the tube was replaced by nitrogen, no absorption occurred, and the cresol in the tube did not darken even after three years' exposure to light. In another series of experiments, the flask containing the benzene solution of cresol and the copper was connected with a gas burette containing oxygen saturated with benzene over mercury, and the decrease in the volume was measured in the usual way. Here, too, the initial delay in the absorption was noticed, and this was attributed either to the presence of a substance retarding the oxidation or to the necessity of the formation of a catalytic compound. In support of the former view was the fact that the oxidation proceeded more consistently when the oxygen derived from potassium chlorate was replaced by electrolytic oxygen freed from all traces of ozone. Green crystals containing 44.9% of copper (after drying at 100°) were present in the dark liquid after the oxidation. As this amount of copper does not correspond with the composition of any of the probable compounds, it is possible that the benzene ring is broken during the absorption. A similar oxidation was observed in the case of phenol, but more slowly than with *o*-cresol, and here too the initial stage of very slow absorption was present. [See also *J. Soc. Chem. Ind.*, 1919, 812A.] C. A. M.

Chloropicrin. I. JOHN ADDYMAN GARDNER and FRANCIS WILLIAM FOX (T., 1919, 115, 1188—1194).

Crystallography of Ammonium Picrate and of Potassium Trithionate. HERBERT E. MERWIN (*J. Washington Acad. Sci.*, 1919, 9, 429—431).—The orthorhombic crystals of ammonium

picrate are tabular, acicular, or granular in habit. Optical constants are given; refractive indices (Na) $\alpha=1.508$, $\beta=1.872$, $\gamma=1.908$. There is a change in the optic axial plane for different colours, and at wave-length 541μ the crystals are optically uniaxial. Blades of potassium trithionate crystallised from a hot saturated solution show a slight variation in the angles of the prism. Optical constants are given; refractive indices (Na) $\alpha=1.4934$, $\beta=1.5641$, $\gamma=1.602$. L. J. S.

Mercury Mercaptide Nitrites and their Reaction with the Alkyl Iodides. VII. Chain Compounds of Sulphur (*continued*). SIR PRAFULLA CHANDRA RÂY and PRAFULLA CHANDRA GUHA (T., 1919, 115, 1148—1155).

The Electrolytic Reduction of Phenylacetic Acid. C. MARIE, R. MARQUIS, and BIRCKENSTOCK (*Bull. Soc. chim.*, 1919, [iv], 25, 512—516).—Phenylacetic acid can be reduced by electrolytic methods in a sulphuric acid solution, using a lead cathode. The yield is small, owing to a portion of the phenylethyl alcohol formed combining with the sulphuric acid and being subsequently oxidised at the anode. The only portion of the alcohol which escapes this destruction is that which, at the moment of its formation, combines with the excess of phenylacetic acid present. W. G.

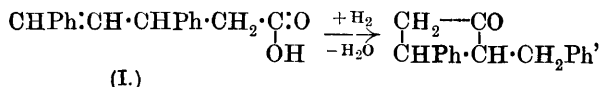
Syntheses of Naphthyl-lactic and Naphthylcinnamic Acids. I. β -Phenyl- β - α -naphthyl-lactic Acid and β - α -Naphthylcinnamic Acid. REMO DE FAZI (*Gazzetta*, 1919, 49, i, 242—251).— β -Phenyl- β - α -naphthyl-lactic acid, $C_{10}H_7 \cdot CPh(OH) \cdot CH_2 \cdot CO_2H$, obtained as ethyl ester by decomposing by means of acidified water, the complex, $C_{10}H_7 \cdot CPh(O \cdot ZnBr) \cdot CH_2 \cdot CO_2Et$, formed by the interaction of phenyl α -naphthyl ketone and ethyl bromoacetate in presence of zinc dust, crystallises in slender, colourless, silky needles of peculiar odour, m. p. 188—189°, and with concentrated sulphuric acid in the cold gives a transitory, green coloration changing to reddish-brown. Its *ethyl* ester forms tufts of slender, white needles, m. p. 95—96°, and gives the same colorations with sulphuric acid as the free acid.

β - α -Naphthylcinnamic acid, $C_{10}H_7 \cdot CPh \cdot CH \cdot CO_2H$, obtained as ethyl ester by dehydrating ethyl β -phenyl- β - α -naphthyl-lactate in benzene solution by means of phosphoric oxide, forms silky, white needles, m. p. 219—220°. With concentrated sulphuric acid it first gives a transitory, emerald-green coloration, and then dissolves to a reddish-brown solution with a green fluorescence; on addition of water, the acid solution becomes yellow and yields a precipitate, which is probably the corresponding indone. The *ethyl* ester forms a pale yellow oil, b. p. 278—281°/2 mm., or shining needles, m. p. 69—71° (?), and with concentrated sulphuric acid gives a transitory, green coloration, rapidly changing to reddish-brown.

T. H. P.

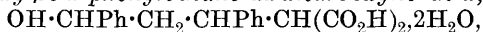
Asymmetric Replacement in the meta-Series. I. WILLIAM HENRY GOUGH and JOCELYN FIELD THORPE (T., 1919, 115, 1155—1164).

Some Factors bearing on 1:6-Addition. TENNEY L. DAVIS (*J. Amer. Chem. Soc.*, 1919, **41**, 1132—1140).—In all the cases in which addition in the 1:6-position has been observed, the unsaturated compound has also had an ethylenic linking in the 3:4-position (compare Straus, A., 1910, i, 119). The author has now synthesised the compound (I) without this disturbing element, but finds that it is abnormal in behaviour. When reduced, for example, it was expected to yield a ketone, thus:



but it could not be reduced either by zinc and acetic acid or sodium amalgam.

Phenyl styryl ketone is condensed with methyl or ethyl malonate (Kohler, A., 1911, i, 984), the esters are hydrolysed, and the ketonic acid is reduced by means of sodium amalgam. Two by-products of the reduction are mentioned, namely, *βδ-diphenylvalerolactone*, $\text{O} \langle \underset{\text{CO---CH}_2}{\text{CHPh}\cdot\text{CH}_2} \rangle \text{CHPh}$, needles, m. p. 113—114°, and *δ-hydroxy-βδ-diphenylbutane-αα-dicarboxylic acid*,



nodules of stout needles, m. p. 190—195° (decomp.), but the chief product is *δ-hydroxy-βδ-diphenylvaleric acid*, which crystallises with 0.5H₂O, in needles from benzene or pearly flakes from alcohol, m. p. 154—154.5°. When boiled with acetic anhydride and a little sulphuric acid, this compound changes into the desired unsaturated acid, accompanied in one experiment by an *internal ester*, $\text{O} \langle \underset{\text{CO}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CHPh}}{\text{CHPh}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}} \rangle \text{O}$, m. p. 92—94°.

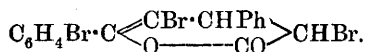
βδ-Diphenyl-Δ⁴-butene-α-carboxylic acid (I) crystallises from benzene in colourless, rhombic needles, m. p. 124—125°, and forms a *methyl ester*, clusters of stout needles, m. p. 47—48°, which reacts with magnesium phenyl bromide to form the *carbinol*, $\text{CHPh}\cdot\text{CH}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CPh}_2\cdot\text{OH}$, in thin needles, m. p. 138—139°. J. C. W.

The cycloPropane Series. V. E. P. KOHLER and L. L. STEELE (*J. Amer. Chem. Soc.*, 1919, **41**, 1093—1105. Compare A., 1917, i, 566—570; 1918, i, 72; this vol., i, 404).—All the *cyclopropane* derivatives described in the earlier papers have had two carboxyl groups (or ester groups) attached to one of the ring carbon atoms. The authors have now attempted to prepare monocarboxylic acids of this series, but have encountered great difficulties before achieving a measure of success.

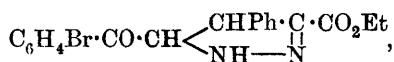
In the first place, benzoylphenyl*cyclopropane*dicarboxylic acid loses carbon dioxide on heating, but the yield of the monocarboxylic acid is insignificant, no matter what modifications of the treatment are tried (compare A., 1917, i, 566).

A second scheme is based on the elimination of hydrogen bromide

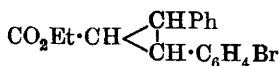
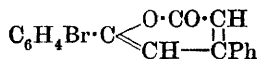
from an α -bromo-ketonic ester. γ -p-Bromobenzoyl- β -phenylbutyric acid, $\text{C}_6\text{H}_4\text{Br}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, needles, m. p. $152-153^\circ$, is prepared by heating the corresponding malonic acid (A., 1918, i, 72), converted into the methyl ester, stout needles, m. p. 93° , and this is brominated. Methyl γ -bromo- γ -p-bromobenzoyl- β -phenylbutyrate is obtained in two forms, chiefly slender needles, m. p. $81-82^\circ$, but also long, feathery crystals, m. p. 92° . When it is heated with potassium acetate in methyl alcohol, the product is not a cyclopropane derivative, but γ -p-bromobenzoyl- β -phenylbutyrolactone, $\text{C}_6\text{H}_4\text{Br}\cdot\text{CO}\cdot\text{CH}\begin{smallmatrix} \text{O} \\ \diagup \end{smallmatrix}\text{CO} \\ \text{CHPh}\cdot\text{CH}_2$, colourless needles, m. p. 158° . The same lactone may be obtained by the action of sodium carbonate on γ -bromo- γ -p-bromobenzoyl- β -phenylbutyric acid, $\text{C}_6\text{H}_4\text{Br}\cdot\text{CO}\cdot\text{CHBr}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, m. p. $146-147^\circ$, this being formed by the bromination of the above free butyric acid derivative. In addition, when this γ -bromo-acid is warmed with phosphorus tribromide and bromine, it yields a compound which crystallises in large, rhombic crystals, like smoky quartz, and is probably represented by the formula



The successful scheme is an adaptation of Buchner's method for preparing cyclopropane acids from pyrazolines. $\alpha\beta$ -Unsaturated ketones are condensed with ethyl diazoacetate to give ketonic pyrazolines, and these are heated. The chief product is a pyrone, but a yield of about 40% of a cyclopropane derivative may be obtained if the decomposition is carried out in the presence of platinum scrap. In the preliminary trials of this scheme, p-bromophenyl styryl ketone was used. When heated with ethyl diazoacetate at $95-175^\circ$, this yields an ester which may be hydrolysed to 5-p-bromobenzoyl-4-phenylpyrazole-3-carboxylic acid, $\text{C}_6\text{H}_4\text{Br}\cdot\text{CO}\cdot\text{C}\begin{smallmatrix} \text{CPh}\cdot\text{C}\cdot\text{CO}_2\text{H} \\ \text{NH}-\text{N} \end{smallmatrix}$, feathery needles, m. p. $216-217^\circ$ (decomp.), which changes at 245° into 5-p-bromobenzoyl-4-phenylpyrazole, m. p. 159° . If the reaction mixture is diluted with light petroleum, however, the product is the desired ethyl 5-p-bromobenzoyl-4-phenylpyrazoline-3-carboxylate,



rhombic plates, m. p. $150-154^\circ$ (decomp.). This loses nitrogen at $170-200^\circ$, changing into a mixture of 6-p-bromophenyl-4-phenyl-1:2-pyrone, feathery crystals, m. p. 183° , and a trace of ethyl 3-p-bromophenyl-2-phenylcyclopropane-1-carboxylate, needles, m. p. $118-119^\circ$.

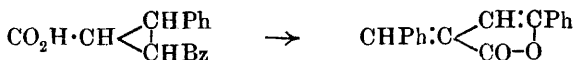


In the main experiments, unsubstituted phenyl styryl ketone was

used. This reacts with ethyl diazoacetate as above to form *ethyl 5-benzoyl-4-phenylpyrazoline-3-carboxylate*. This crystallises in hexagonal plates, m. p. 156—158°, which change when kept for some time just below the decomposition temperature into an *isomeride*, needles, m. p. 102·5—103°. Both forms, in alcoholic solution, give a vivid red colour with a trace of hydrogen chloride. When heated alone at a high temperature, the product consists almost entirely of 4:6-diphenyl-1:2-pyrone, yellow plates, m. p. 138—139°, but in the presence of platinum, at 220—225°, a 37% yield of *ethyl 3-benzoyl-2-phenylcyclopropane-1-carboxylate* is obtained. This crystallises in thin plates, m. p. 103°, is stable at 300°, and does not reduce an acetone solution of permanganate.

The free acid, $\text{CO}_2\text{H}\cdot\text{CH}\begin{smallmatrix} \text{CHPh} \\ \text{CHBz} \end{smallmatrix}$, as obtained by hydrolysis with aqueous-alcoholic potassium hydroxide in the cold, exists in two stereoisomeric forms, slender needles, m. p. 176°, and long threads, m. p. 147—150°, the latter being the more soluble in benzene, and yielding an isomeric *ethyl ester*, m. p. 93—94°, when its silver salt is treated with ethyl iodide.

It is interesting to compare the new acid and ester with Buchner's 2-phenylcyclopropane-1:3-dicarboxylic acid and the 3-benzoyl-2-phenylcyclopropane-1:1-dicarboxylic acid of the earlier papers. The new acid is decomposed when heated with hydrobromic acid in a sealed tube, whereas Buchner's acid is quite stable. When left with hydrogen bromide dissolved in acetic acid, however, it suffers rupture of the ring between carbon atoms 2 and 3, like the 1:1-dicarboxylic acid, only more readily, the product being γ -phenyl- α -benzylidenecrotonolactone, thus:

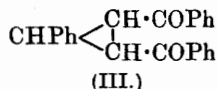
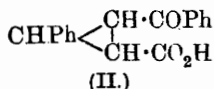
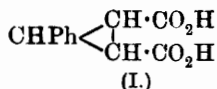


(see A., 1917, i, 566). Hydrochloric acid under the same conditions gives an unstable *acid*, $\text{CHPhCl}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\text{Bz}$, m. p. 131—132°, which changes above its m. p. into β -benzylidenepropiophenone, $\text{CHPh}\cdot\text{CH}\cdot\text{CH}_2\text{Bz}$. The corresponding ester, *ethyl β -chloro- α -phenacyl- β -phenylpropionate*, hexagonal plates, m. p. 68—69°, is stable, and may be obtained most readily by the action of alcoholic hydrogen chloride on the cyclic acid or its ester. The cyclic ester also behaves as an unsaturated compound towards zinc and acetic acid, being reduced to the ester of γ -benzoyl- β -phenylpropionic acid. A great difference between methyl 3-benzoyl-2-phenylcyclopropane-1-carboxylate and the 1:1-dicarboxylates, however, lies in their behaviour towards basic agents. The latter are most easily ruptured between the carbon atoms 1 and 3, but the new ester is indifferent to dry alkyl oxides, and no means of effecting the same opening of the ring have been found.

ω -Nitrostyrene also reacts very vigorously with ethyl diazoacetate, but the primary nitropyrazoline loses nitrous acid so readily that it changes spontaneously into *ethyl 4-phenylpyrazole-3-carboxylate*, plates, m. p. 164—165°. The corresponding *acid*,

$\text{CO}_2\text{H}\cdot\text{C} \begin{smallmatrix} \text{CPh}\cdot\text{CH} \\ \text{N} \text{---} \text{NH} \end{smallmatrix}$ m. p. 252—253°, changes into 4-phenylpyrazole when heated above 250°. J. C. W.

The cycloPropane Series. VI. E. P. KOHLER and W. N. JONES (*J. Amer. Chem. Soc.*, 1919, **41**, 1249—1263).—In the last paper (preceding abstract) a comparison was made between the properties of the *cyclopropanedicarboxylic acid* (I) and the ketonic acid (II). The diketone (III) has now been synthesised and studied in the same manner.



Benzylidenediacetophenone (Kostanecki, A., 1896, i, 556) reacts with bromine in slightly warmed chloroform to give two products, according to the proportion of bromine, namely, *β-bromo-αγ-triphenylpentane-αε-dione*, $\text{COPh}\cdot\text{CHBr}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{COPh}$, m. p. 131° (decomp.), and *βδ-dibromo-αγ-triphenylpentane-αε-dione*, m. p. 149° (decomp.). Both substances may be converted into 1:2-dibenzoyl-3-phenylcyclopropane, the former by treatment with sodium ethoxide solution, giving a modification which crystallises in needles, m. p. 116°, the latter by boiling with alcoholic potassium iodide, giving an isomeride which has m. p. 151°, but changes into the form with m. p. 116° on crystallisation from alcohol containing 1% of sodium hydroxide. Both forms of the diketone yield the same *monoxime*, m. p. 144°, and *dioxime*, needles, m. p. 175°.

The diketone is remarkably sensitive to reducing agents. When boiled with moist alcohol and zinc dust, it forms the parent benzylidenediacetophenone, the ring being opened at the point where it was originally closed.

Unlike the ketonic acid (II), the diketone does not react with alcoholic solutions of hydrogen chloride or bromide. With glacial acetic acid solutions, however, it behaves like other *cyclopropane* derivatives described in this series of papers, the ring being opened between the carbon atoms 2 and 3. The resulting 1:4-diketone then loses water and changes, as usual, into a furan derivative. Thus, with a solution of hydrogen bromide, the product is 2:5-diphenyl-4-*α*-bromobenzylfuran, $\text{O} \begin{smallmatrix} \text{CPh}\cdot\text{C}\cdot\text{CHBrPh} \\ \text{CPh}\cdot\text{CH} \end{smallmatrix}$, greenish-yellow

prisms, m. p. 110°. This is capable of yielding a number of reactive substances, through which it may ultimately be converted into 2:5-diphenylfuran, and thus identified. With potassium acetate and acetic acid, for example, it forms 2:5-diphenyl-4-*α*-acetoxybenzylfuran, yellow needles, m. p. 84°, which may be hydrolysed by alcoholic hydrochloric acid to 2:5-diphenyl-4-*α*-hydroxybenzylfuran. This may also be obtained by the action of sodium methoxide solution on the bromobenzyl compound. It

crystallises in needles, m. p. 105° , and may be oxidised by chromic acid in cold acetic acid solution to a *product*, $C_{23}H_{18}O_3 \cdot H_2O$, m. p. 89° , which readily loses $1H_2O$ at 110° , or $2H_2O$ when boiled with alcoholic potassium hydroxide, methyl-alcoholic hydrogen chloride, or acetic anhydride and sodium acetate, giving 4-benzoyl-2:5-diphenylfuran, which crystallises in yellow needles, and forms a 3-bromo-compound, m. p. 120° , when treated with bromine in chloroform. The *oxime* of the benzoyl derivative crystallises in rosettes of needles, m. p. 174° , and readily undergoes the Beckmann transformation to 2:5-diphenylfuran-4-carboxylanilide,

$O \begin{array}{l} \text{CPh} \cdot \text{C} \cdot \text{CO} \cdot \text{NHPh} \\ \text{CPh} \cdot \text{CH} \end{array}$, colourless needles, m. p. 187° . This is

hydrolysed by alcoholic potassium hydroxide to the known 2:5-diphenylfuran-4-carboxylic acid, m. p. 217° , which changes into 2:5-diphenylfuran when distilled with zinc dust.

The cyclic diketone reacts with Grignard agents without rupture of the ring, giving ditertiary alcohols. 3-Phenyl-1:2-di-diphenylcarbinolcyclopropane, $CHPh \begin{array}{l} \text{CH} \cdot \text{CPh}_2 \cdot \text{OH} \\ \text{CH} \cdot \text{CPh}_2 \cdot \text{OH} \end{array}$, crystallises in clusters of slender needles, m. p. 183° , and 3-phenyl-1:2-di- α -phenyl- α -ethylcarbinolcyclopropane has m. p. 129° .

The diketone reacts with phosphorus pentachloride in boiling benzene to form $\alpha\delta$ -dichloro- γ -benzoyl- $\alpha\delta$ -diphenyl- Δ^{γ} -butene, $CHPhCl \cdot CHBz \cdot CH \cdot CPhCl$, m. p. 122° , which is transformed into α -chloro- γ -benzoyl- $\alpha\delta$ -diphenyl- Δ^{γ} -butadiene, prisms, m. p. 84° , when boiled with methyl-alcoholic potassium acetate. The latter compound reacts with magnesium phenyl chloride to give α -chloro- γ -benzoyl- $\alpha\delta\delta$ -triphenyl- Δ^{γ} -butene, $CHPh_2 \cdot CHBz \cdot CH \cdot CPhCl$, in large, colourless prisms, m. p. 140° .

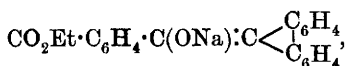
The action of bromine in warm chloroform on the cyclic diketone is somewhat obscure, but the *product*, $C_{23}H_{18}O_2Br_2$, m. p. 129° (decomp.), is isomeric with the dibromide obtained in the first instance from benzylidenediacetophenone, since it yields the same compounds when treated with potassium iodide or alcoholic potassium acetate. In the latter reaction, the product is either 2-bromo-1:2-dibenzoyl-3-phenylcyclopropane, needles, m. p. 122° , or 2-acetoxy-1:2-dibenzoyl-3-phenylcyclopropane, m. p. 159° , according to the proportion of potassium acetate employed. The latter could not be hydrolysed to the hydroxy-derivative. Alkaline agents give oily residues, whilst treatment with alcoholic hydrogen chloride results in the formation of 2-benzoyl-3:5-diphenylfuran, which crystallises in plates, m. p. 118° , forms a 4-bromo-derivative, m. p. 110° , and may be reduced by means of zinc and acetic acid to 3:5-diphenyl-2-benzylfuran, bright yellow needles, m. p. 193° . The *oxime* of the benzoyl compound, m. p. 152° , suffers the Beckmann transformation to 3:5-diphenylfuran-

2-carboxylanilide, $\begin{array}{l} \text{CH} \cdot \text{CPh} \cdot \text{O} \\ \text{CHPh} = \text{C} \cdot \text{CO} \cdot \text{NHPh} \end{array}$, m. p. 143° , and this may be hydrolysed to 3:5-diphenylfuran-2-carboxylic acid, m. p. 194°

(decomp.). This acid yields the known 3:5-diphenylfuran when distilled with zinc dust (Engler and Dengler, A., 1893, i, 512).

J. C. W.

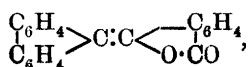
Condensation of Ethyl Phthalate with Fluorene. WILHELM WISLICHENUS and PETER NEBER (*Annalen*, 1919, **418**, 274—293).—A mixture of fluorene (1 mol.), sodium (1 atom), and ethyl phthalate (about 1.14 mols.) is heated on the water-bath until the sodium has disappeared, and is then treated, after cooling, with benzene and ice, whereby the *sodium* derivative of ethyl fluorene-phthaloylate (*o*-carbethoxyphenyl fluorenyl ketone),



yellowish-white needles with $5\text{H}_2\text{O}$, is obtained, which is remarkably stable to boiling dilute alkali hydroxide solution. In aqueous solution it is decomposed by carbon dioxide or dilute hydrochloric acid, yielding the α -modification, $\text{CO}_2\text{Et} \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{OH}) : \text{C} \begin{array}{c} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{array}$, of *o*-carbethoxyphenyl fluorenyl ketone, microscopic prisms, m. p. 217—218°; lower m. p.'s, dependent on the method of crystallisation, are frequently obtained in consequence of partial conversion into the β -modification. The α -modification does not react with ferric chloride, but it decolorises bromine in alcoholic solution and forms a *copper* derivative, $(\text{C}_{23}\text{H}_{17}\text{O}_3)_2\text{Cu} \cdot \text{H}_2\text{O}$, bluish-green needles, m. p. about 180°; by bromination in chloroform in the presence of a little phosphorus pentabromide, it yields *o*-carbethoxyphenyl 9-bromofluorenyl ketone, $\text{CO}_2\text{Et} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CBr} \begin{array}{c} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{array}$, colourless prisms, m. p. 190—191°.

By keeping for several weeks, the α -modification changes into the stable β -modification, $\text{CO}_2\text{Et} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CH} \begin{array}{c} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{array}$, colourless leaflets or prisms, m. p. 140—141°. The change is effected more rapidly by distillation in a vacuum, by heating at 220°, or, most simply, by boiling with alcohol. The conversion of the β - into the α -modification is effected, through the sodium derivative, by means of alcoholic sodium hydroxide solution. The β -modification does not form a copper derivative and does not react with bromine in alcoholic solution. Both modifications are remarkably stable to alkalis; they are only decomposed by an excess of alcoholic alkali at 150°, yielding ethyl alcohol, alkali phthalate, and fluorene.

By heating above 220°, by distillation in a vacuum or, best, by heating with potassium hydrogen sulphate at 230°, either modification is converted into *phthalylfluorene*, yellow, flattened needles, m. p. 204—206°. To this substance is ascribed, not the indanedi-one formula, but the asymmetric constitution,

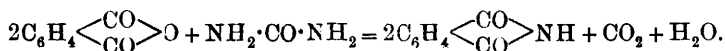


in order to account for its intense yellow colour, its easy decomposition by alkalis into *fluorenephthaloylic acid* (*o*-carboxyphenyl *fluorenyl ketone*), $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}<\text{C}_6\text{H}_4$, colourless crystals, m. p. 188—189° (yellow *dipotassium salt*, $\text{C}_{21}\text{H}_{12}\text{O}_3\text{K}_2$), and its conversion in boiling alcoholic solution by an excess of hydrazine hydrate into fluorene and phthalylhydrazide. It can also be prepared by heating a mixture of phthalic anhydride, fluorene, and anhydrous potassium acetate at 200—220°.

The *hydrazide*, $\text{NH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}<\text{C}_6\text{H}_4$, glassy plates, prepared by shaking a suspension of phthalylfluorene in alcohol with hydrazine hydrate, does not melt below 200° when examined in the usual manner, but melts with decomposition (loss of water) when placed in a bath heated at 190°, and then resolidifies. When heated for half an hour at 220°, it is converted into 1-*fluorenyl-phthalazone*, $\text{C}_6\text{H}_4>\text{CH}\cdot\text{C}<\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{N}=\text{N}$, leaflets, m. p. 275—277°.

Phthalylfluorene is reduced to *o*-*fluorenylmethylbenzoic acid*, $\text{C}_6\text{H}_4>\text{CH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, groups of faintly yellow needles, m. p. 185—186°, by heating with fuming hydriodic acid and amorphous phosphorus at 160° for eight hours. C. S.

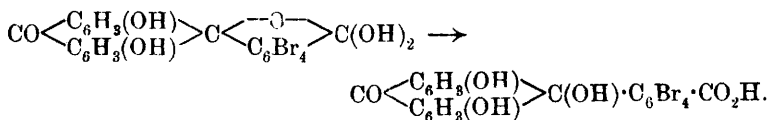
Method for the Preparation of Phthalimide. WALTER HERZOG (*Zeitsch. angew. Chem.*, 1919, **32**, 301).—Phthalic anhydride (2 mols.) and carbamide (1 mol.) are heated together in a long-necked flask; reaction commences at 130° to 135°, and the temperature rises to 150° without further external heating. At the end of the reaction, the liquid mass solidifies suddenly. When cold, the porous solid is washed with a small quantity of water and dried; it consists of practically pure phthalimide m. p. 230—231°, the yield being 90% or more of the amount required by the equation



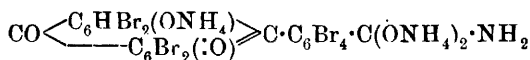
A similar reaction takes place between thiocarbamide and phthalic anhydride, but not between carbamide and succinic anhydride, citraconic anhydride, or camphoric anhydride. W. P. S.

Phthalic Acid Derivatives; Constitution and Colour.
XVII. Tetrabromofluorescein, Tetrabromoeosin, and some of their Derivatives. DAVID S. PRATT, G. F. HUTCHINSON, and A. W. HARVEY (*J. Amer. Chem. Soc.*, 1919, **41**, 1293—1297).—Compare the analogous iodine compounds, A., 1918, i, 175. Tetrabromofluorescein, $\text{C}_{20}\text{H}_6\text{O}_5\text{Br}_4$, dissolves in alkali hydroxides with about the same colour as fluorescein, and is precipitated as a yellow *hydrate* on the addition of an acid. When this is dried in

a steam-oven, the brick-red, quinonoid form of tetrabromofluorescein is left, but this changes into the yellow, benzenoid form when wetted with acetone or ethyl acetate. The hydrate changes into the very pale yellow *tetrabromofluoresceincarbinolcarboxylic acid* when treated with alcohol, thus:



Anhydrous tetrabromofluorescein forms a bright red *diammonium* salt and a colourless *diacetate*, and reacts with bromine to give *octabromofluorescein* (tetrabromoeosin). This is almost colourless, but so sensitive to alkalis that it is generally faintly pink. It dyes silk an attractive pink shade, and forms a *diacetate*, crystallising with $1\text{C}_6\text{H}_6$, and a *tetra-ammonium* salt, of a brilliant, deep bronze colour, probably represented by the formula



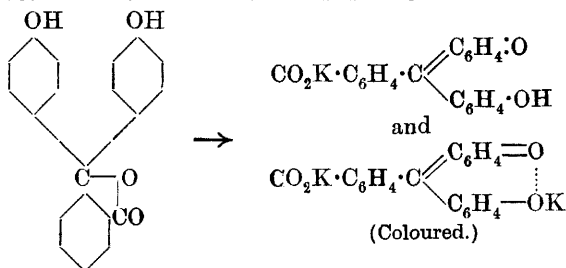
J. C. W.

Phthalic Acid Derivatives; Constitution and Colour.
XVI. Phenoltetrabromophthalein and some of its Derivatives. DAVID S. PRATT, F. B. DOANE, and A. W. HARVEY (*J. Amer. Chem. Soc.*, 1919, **41**, 1289—1293. Compare A., 1918, i, 167—172, 175—177, 540—541).—Tetrabromophthalic anhydride (*ibid.*, 540) condenses with phenol in the presence of fuming sulphuric acid (15% SO_3) to form *tetrabromofluoran*, $\text{C}_{20}\text{H}_8\text{O}_3\text{Br}_4$, colourless crystals, insoluble in alcohol, and a 75% yield of *phenoltetrabromophthalein*, $\text{C}_{20}\text{H}_{10}\text{O}_4\text{Br}_4$, which is nearly white, gives colourless solutions in most solvents, is indifferent to ammonia, but very sensitive to alkali hydroxides. The phthalein yields a colourless, crystalline *diacetate*, *dibenzoate*, and *dimethyl ether*, and may be brominated in boiling alcohol. *Tetrabromophenoltetrabromophthalein*, $\text{C}_{20}\text{H}_6\text{O}_4\text{Br}_8$, forms very pale yellow crystals, dissolves in alkali hydroxides with a brilliant blue colour, reacts with ammonia gas to give a turquoise-blue *diammonium* salt, and yields a colourless *diacetate* and *dibenzoate*, which both crystallise with one molecular proportion of benzene.

J. C. W.

The Quinone-Phenolate Theory of Indicators. The Reactions of Phenolsulphonphthalein and its Bromo- and Nitro-derivatives, and their Monobasic and Dibasic Salts. E. C. WHITE and S. F. ACREE (*J. Amer. Chem. Soc.*, 1919, **41**, 1190—1212. Compare A., 1918, ii, 328; this vol., ii, 400).—In the theory of indicators developed by Acree, it is held that the production of colour in the case of phenolphthalein does not begin when the lactone ring is opened, but when quinone-phenolate ions

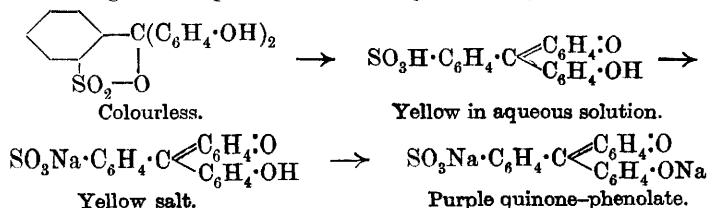
are formed. That is, phenolphthalein is regarded as a substance which gives colourless mono-acid and dark red di-acid salts, thus:



The existence of the intermediate salts has now been established in the case of phenolsulphonphthalein, and it is also shown that other factors than the further addition of alkali which tend to increase the production of quinone-phenolate ions, such as nitration or bromination of the indicator, operate to cause intense colour changes.

For the production of phenolsulphonphthalein, "saccharin" is hydrolysed by means of dilute hydrochloric acid (400 grams; 500 c.c. conc. HCl; 6—7 litres of water), and the ammonium hydrogen *o*-sulphobenzoic acid is allowed to crystallise after concentration (to 600 c.c.). The salt is finely powdered, thoroughly wetted with thionyl chloride, and heated for a few hours, when the excess of reagent is distilled off under reduced pressure and the residual cake is broken up and extracted with benzene. The pure *o*-sulphobenzoic anhydride is heated with phenol at 130—135° for six hours, when the excess of phenol is removed in steam, the residue is dissolved in alkali hydroxide, filtered, and the phenolsulphonphthalein is precipitated by an acid.

Phenolsulphonphthalein dissolves in boiling water to the extent of about 0.03 gram per 100 c.c. The solution is orange-coloured, since it contains the free quinonoid sulphonic acid. On the addition of pure sodium hydroxide solution, a purple streak appears locally, but this disappears on shaking, and is not permanent until nearly one equivalent of alkali has been added. That is, a salt of the quinonoid sulphonic acid is being formed having the same colour as the acid, and at last, when the ionisation of the sulphonic group is so depressed that phenolate ions appear, then the striking colour change takes place. The changes are represented thus:



The *mono-potassium*, *mono-silver*, and *mono-calcium* salts have been isolated; they all give orange solutions, which become purple

on the addition of alkali hydroxides. When left in an atmosphere of ammonia, phenolsulphonphthalein also forms an almost black *diammonium* salt, which dissolves with purple colour, and changes into a red *mono-ammonium* salt when left over sulphuric acid in a desiccator.

Tetrabromophenolsulphonphthalein is conveniently obtained by slowly adding bromine to a solution of the indicator in acetic acid maintained near its boiling point. The crystals are almost colourless when moistened with acetic acid, but acquire a flesh-pink colour when dried. When heated, it gives a green sublimate at 210° , becomes deeper orange in colour, and finally melts at $270\text{--}271^{\circ}$ (decomp.). The *di-ammonium* salt is stable in the neighbourhood of sulphuric acid, owing to the increased acidity of the phenol group. *Tetranitrophenolsulphonphthalein*, canary-yellow, minute flakes, decomp. above 200° , also forms a stable *di-ammonium* salt. The tetrabromo-compound dissolves in water (0.7 gram per litre), giving a dark red solution, which becomes deep blue on diluting or adding a trace of alkali, but gradually yellow on adding a strong acid. The tetranitro-compound gives purple-red solutions in water, which are not visually or spectroscopically altered by the addition of small amounts of alkali, but gradually become yellow on adding acids, the solution changing to purple once more on dilution. Owing to the presence of nitro-groups or bromine atoms in the phenolic components, the production of the coloured quinone-phenolate ions is rendered easy, and considerable concentrations of hydrogen ions must be present before their ionisation is depressed.

Phenolsulphonphthalein and its tetrabromide have been treated with diazomethane. The *products*, m. p. 158° and m. p.

$234\text{--}235^{\circ}$, appear to be esters of the type $\text{SO}_3\text{Me}\cdot\text{C} \begin{smallmatrix} \text{C}_6\text{H}_4\cdot\text{O} \\ \text{C}_6\text{H}_4\cdot\text{OMe} \end{smallmatrix}$

but they are remarkably stable towards alkalis, and must be investigated more fully.

It is stated that stannic chloride is an excellent agent for the condensation of phthalic anhydride and phenols. J. C. W.

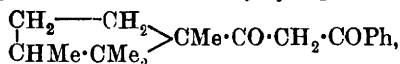
Optically Active Ketones : Ketones of 1:2:2:3-Tetramethylcyclopentane. H. RUPE and C. A. KLOPPENBURG (*Helv. Chim. Acta*, 1919, **2**, 363—378).—1-Acetyl-1:2:2:3-tetramethylcyclopentane (1:2:2:3-tetramethylcyclopentyl methyl ketone),

$\text{CMe}_2 \begin{smallmatrix} \text{CHMe}-\text{CH}_2 \\ \text{CMeAc}\cdot\text{CH}_2 \end{smallmatrix}$, prepared by treating the chloride of campholic acid (1:2:2:3-tetramethylcyclopentane-1-carboxylic acid) with either zinc methyl or ethyl sodiomalonate or ethyl sodioacetoacetate, and purified by means of its semicarbazone, is a colourless, mobile oil with a persistent cedar-wood oil odour, b. p. $93\text{--}95^{\circ}/10\text{ mm.}$, D_4^{20} 0.9163, $[\alpha]_D^{20} + 51.27^{\circ}$, $[\alpha]_D^{20} + 63.67^{\circ}$, $[\alpha]_{\text{Hf}}^{20}$ ($\lambda = 546.3\text{ }\mu\mu$) $+ 74.17^{\circ}$, and $[\alpha]_F^{20} + 93.32^{\circ}$; in benzene solution these rotations are respectively 43.45° , 53.89° , 62.06° , and 77.49° . The semicarbazone has m. p. 226° (decomp.) (Meerwein, this vol., i, 162, gave m. p. 232°); the *oxime*, m. p. 69.5° , the *p-nitrophenyl-*

hydrazone, m. p. 134° , the *benzylidene* derivative, m. p. 45° , D_4^{20} 0.8896 , $[\alpha]_C^{20} + 44.29^{\circ}$, $[\alpha]_D^{20} + 54.29^{\circ}$, $[\alpha]_{H_g}^{20} + 61.49^{\circ}$, $[\alpha]_F^{20} + 69.36^{\circ}$ (in benzene), and the *anisylidene* derivative, m. p. 54° , D_4^{20} 0.8924 , $[\alpha]_C^{20} + 50.65^{\circ}$, $[\alpha]_D^{20} + 63.43^{\circ}$, $[\alpha]_{H_g}^{20} + 74.07^{\circ}$, $[\alpha]_F^{20} + 90.54^{\circ}$, were prepared.

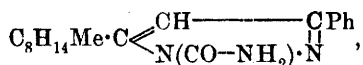
1:2:2:3-Tetramethylcyclopentyl ethyl ketone, $C_{12}H_{22}O$, prepared by the action of either zinc ethyl iodide or zinc ethyl on the acid chloride of 1:2:2:3-tetramethylcyclopentane-1-carboxylic acid, forms a colourless oil of aromatic odour, b. p. $104^{\circ}/10$ mm., D_4^{20} 0.9124 , $[\alpha]_C^{20} + 50.64^{\circ}$, $[\alpha]_D^{20} + 63.15^{\circ}$, $[\alpha]_{H_g}^{20} + 73.89^{\circ}$, $[\alpha]_F^{20} + 94.08^{\circ}$. It does not condense with semicarbazide or hydroxylamine, but yields a *p*-nitrophenylhydrazone, m. p. 201° .

1-Benzoylacetyl-1:2:2:3-tetramethylcyclopentane,



prepared either by the condensation of ethyl 1:2:2:3-tetramethylcyclopentane-1-carboxylate with sodioacetophenone or by the action of ethyl benzoate on 1:2:2:3-tetramethylcyclopentyl methyl ketone, forms a viscous, yellow, odourless oil, b. p. $205^{\circ}/10$ mm., D_4^{20} 1.0500 , $[\alpha]_C^{20} + 50.19^{\circ}$, $[\alpha]_D^{20} + 63.83^{\circ}$, $[\alpha]_{H_g}^{20} + 76.08^{\circ}$, $[\alpha]_F^{20} + 100.92^{\circ}$; in benzene, the respective rotations are 45.07° , 57.26° , 68.22° , and 90.25° . Its alcoholic solution gives an intense red coloration with ferric chloride. With phenylhydrazine it forms the *diphenylated*

pyrazole, $C_8H_{14}Me \cdot C \begin{array}{c} \text{CH} \cdot \text{CPh} \\ \text{N} - \text{NPh} \end{array}$ or $C_8H_{14}Me \cdot C \begin{array}{c} \text{CH} - \text{CPh} \\ \text{NPh} \cdot \text{N} \end{array}$, which crystallises in long, white, felted needles, m. p. 142° , and becomes highly electrified when rubbed. With semicarbazide it gives the compound, $C_8H_{14}Me \cdot C \begin{array}{c} \text{CH} \cdot \text{CPh} \\ \text{N} - \text{N} \cdot \text{CO} \cdot \text{NH}_2 \end{array}$ or



which forms short, apparently monoclinic, white prisms.

A simple method of preparing zinc methyl in large quantities by the action of a zinc-copper couple on methyl iodide in a steel bomb is described.

T. H. P.

Relations between the Ionones and Irone. L. RUZICKA (*Helv. Chim. Acta*, 1919, 2, 352—363).—The reduction of irone by hydrogen in presence of colloidal palladium or platinum black yields tetrahydroirone, an exact chemical proof being thus furnished of the presence of two double linkings in the irone molecule. According to the formulæ for α - and β -ionones and irone, the tetrahydro-derivatives of these compounds should be identical, except as regards optical activity. The two ionones do, indeed, yield the same tetrahydro-product (compare Skita, A., 1913, i, 63), but tetrahydroirone differs from this, not only by its dextro-rotation, but by its higher density and higher boiling point. Assuming the same structural formula, such differences can depend only on *cis*-

trans isomerism; the boiling-point difference, namely, $14^{\circ}/13$ mm., is higher than has been observed in any similar case, and may be conditioned by the relatively long side-chain of the molecules.

The attempts made to establish the structural relations between tetrahydroionone and tetrahydroirone have been unsuccessful. The latter does not undergo racemisation when heated at a high temperature with either hydrochloric acid or alkali. Further, oxidation of the saturated ketones by means of permanganate, as well as oxidation by means of sodium hypobromite of the sodium salts of tetrahydro-iononic and -ironic acids, do not yield the expected products, the formation of large proportions of oxalic acid in all cases indicating that the long side-chain is first oxidised away. Results previously obtained, especially the reaction by which β -ionone is formed, and which consists in the scission of a water molecule, indicate that in the ionones (and tetrahydroionone) the two side-chains, CH_3 and $\text{CH}\cdot\text{CHAc}$, occupy *cis*-positions and in irone (and tetrahydroirone) *trans*-positions at the asymmetric carbon atom.

When irone is reduced in presence of colloidal palladium by means of a limited proportion of hydrogen, only tetrahydro- and not dihydro-irone is formed, and it is uncertain if Skita (*loc. cit.*) obtained dihydroionones in this way, no crystalline derivatives being described by him.

Tetrahydroirone, $\text{CH}_2\langle\begin{smallmatrix} \text{CH}_2-\text{CMe}_2 \\ \text{CH}_2\cdot\text{CHMe} \end{smallmatrix}\rangle\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COMe}$, forms a colourless oil of characteristic cedar-wood odour, b. p. $143\text{--}145^{\circ}/13$ mm., and in carbon disulphide solution decolorises bromine with evolution of hydrogen bromide. The *semicarbazone*, $\text{C}_{14}\text{H}_{27}\text{ON}_3$, forms crystals, m. p. $202\text{--}203^{\circ}$, and gives the ketone again when boiled with potassium hydrogen sulphate solution.

Tetrahydroionol, b. p. $142\text{--}143^{\circ}/17$ mm., $D_{15}^{20} 0.9144$ (Skita, A., 1916, i, 16, gave b. p. $142\text{--}143^{\circ}/20$ mm., $D_{20}^{20} 0.9126$), may be obtained by reducing the ionones by means of hydrogen in ethereal solution containing platinum black, whereas in presence of colloidal palladium the reduction proceeds only as far as tetrahydroionone.

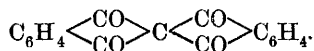
Reduction of α -ionone in 50% aqueous-alcoholic solution by means of hydrogen in presence of Kelber's nickel catalyst (A., 1916, ii, 309) yields *dihydroionol* as an oil, b. p. $135\text{--}140^{\circ}$, so that in this case the reduction of the carbonyl group precedes that of one of the double linkings, probably that in the ring; this appears to be the first instance of such a reaction (compare Rupe, Werder, and Takagi, this vol., i, 27). Dihydroionol does not form a semicarbazone, and on oxidation is converted into *dihydroionone*, $\text{C}_{13}\text{H}_{22}\text{O}$, which is a mobile liquid, b. p. $130\text{--}132^{\circ}/14$ mm., and yields the *semicarbazide*, $\text{C}_{14}\text{H}_{25}\text{ON}_3$, m. p. $166\text{--}168^{\circ}$.

Tetrahydroironic acid, $\text{CH}_2\langle\begin{smallmatrix} \text{CH}_2-\text{CMe}_2 \\ \text{CH}_2\cdot\text{CHMe} \end{smallmatrix}\rangle\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, has b. p. $185\text{--}190^{\circ}/15$ mm., m. p. (crude) about 80° , and *tetrahydroiononic acid*, of the same structural formula, is a viscous oil, b. p. $173\text{--}178^{\circ}/12$ mm. T. H. P.

Diketohydrindene. III. ANANDA KISORE DAS and BROJENDRA NATH GHOSH (*J. Amer. Chem. Soc.*, 1919, **41**, 1221—1225. Compare T., 1915, **107**, 1442; 1916, **109**, 175).—When diketohydrindene is condensed with certain acid anhydrides in the presence of concentrated sulphuric acid, complex, sparingly soluble compounds are formed, which may also be prepared by condensing the anhydrides with anhydrobisdiketohydrindene (Wislicenus and Kötze, A., 1889, 1067), this being, therefore, the primary product in the first reaction. Thus, phthalic anhydride gives the compound, $C_{25}H_{12}O_3$, which crystallises from nitrobenzene in lustrous flakes, m. p. 320° ; benzoic anhydride yields the compound, $C_{25}H_{12}O_3$, golden-yellow needles, m. p. above 320° ; and succinic anhydride forms the compound, $C_{21}H_{10}O_2 \cdot H_2O$, which sublimes without melting at above 316° . The compounds dissolve in hot aniline without forming anilides.

The condensation of diketohydrindene with phthalic anhydride in the presence of acetic anhydride has been described by Marchese (A., 1907, i, 941), who obtained a compound, $C_{26}H_{12}O_5$. This is similar to the above compound, $C_{25}H_{12}O_3$, in outward appearance and m. p., but it differs in that it dissolves freely in sodium hydroxide and is changed on boiling with aniline into a black, crystalline substance, $(C_8H_6O)_x$, m. p. 110° .

The experiment with phthalic anhydride was undertaken in the hope of obtaining a compound of the formula



To this end, ethyl phthalate was made to react with diketohydrindene in the presence of sodium ethoxide, but the product was Schwerin's 2-benzoyl-1:3-diketohydrindene (A., 1894, i, 194) mixed with a little anhydrobisdiketohydrindene. J. C. W.

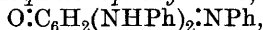
Indophenols and Indamines. II. GUSTAV HELLER (*Annalen*, 1919, **418**, 259—274. Compare A., 1912, i, 916).—It has long been known that indophenols are decomposed by hot dilute mineral acids in the sense of the equation $O:C_6H_4:N \cdot C_6H_4 \cdot OH + H_2O = O:C_6H_4:O + NH_2 \cdot C_6H_4 \cdot OH$. A further change occurs, however, when contact with the mineral acid is maintained for many hours, $2O:C_6H_4:O + 2NH_2 \cdot C_6H_4 \cdot OH = C_6H_4(OH)_2 + O:C_6H_2(NH \cdot C_6H_4 \cdot OH)_2 \cdot O$,

so that the final main products are quinol and dianilinoquinones. The complex substance obtained by the action of hydrochloric acid on the simplest indophenol (*loc. cit.*) is now shown to be 2:5-di-*p*-hydroxyanilino-*p*-benzoquinone by its formation from *p*-benzoquinone and *p*-aminophenol in aqueous-alcoholic solution. In a similar manner, toluquinone yields di-*p*-hydroxyanilinotoluquinone, brown needles, which do not melt below 290° , and *p*-benzoquinone and *as*-dimethyl-*p*-phenylenediamine yield 2:5-di-*p*-dimethylaminoanilino-*p*-benzoquinone. The last compound is not obtained in the decomposition of phenol-blue by hydrochloric acid, because the

dimethylamino-group is replaced by hydroxyl and 2:5-di-*p*-hydroxyanilino-*p*-benzoquinone is formed.

The course of the decomposition of indophenols described above was first elucidated by an investigation of the action of hydrochloric acid (*N*/5) on Bandrowski's base, *p*-benzoquinone-*p*-tolylimide, $\text{O}:\text{C}_6\text{H}_4:\text{N}\cdot\text{C}_7\text{H}_7$, whereby quinol and 2:5-di-*p*-toluidino-*p*-benzoquinone were obtained.

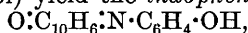
2:5-Dianilino-*p*-benzoquinonephenylimide,



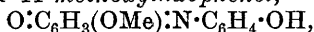
m. p. 202—203°, and 2:5-dianilino-*p*-benzoquinone-*p*-tolylimide, reddish-brown leaflets, m. p. 214°, are obtained by treating *p*-benzoquinonephenylimide and *p*-benzoquinone-*p*-tolylimide respectively with an alcoholic solution of aniline containing a little acetic acid.

After contact with dilute sulphuric acid for three days, Bind-schedler's green yields, amongst other products of the decomposition, tetramethylbenzidine, produced probably by the oxidising action of *p*-benzoquinone on dimethylaniline formed in the reaction.

By oxidation with an alkaline solution of sodium hypochlorite at -10° to -15° , α -naphthol and *p*-aminophenol (but not phenol and 4-amino- α -naphthol) yield the *indophenol*,



crystalline powder, which forms two isomeric *monoanilino*-derivatives, $\text{C}_{22}\text{H}_{16}\text{O}_2\text{N}_2$, m. p. 256° and 181° respectively; guaiacol and *p*-aminophenol yield 11-methoxyindophenol,

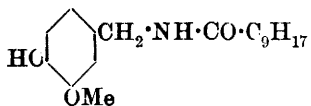


m. p. 181—182° (decomp.) (9:12-dianilino-derivative, m. p. 208—209°), and *m*-chlorophenol and *p*-aminophenol yield 1-chloroindophenol, m. p. 156° (sodium derivative, $\text{C}_{12}\text{H}_7\text{O}_2\text{NClNa}$, needles); the dianilino-derivative, $\text{C}_{24}\text{H}_{18}\text{O}_2\text{N}_3\text{Cl}$, bronze-green needles, m. p. 211—212°, of the last compound is oxidised in alcoholic solution at 60° to the *dianil*, red prisms, m. p. 212—213°, by chromic and acetic acids.

4-Anilino-4'-hydroxydiphenylamine, $\text{NHPh}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, silvery scales, m. p. 145°, is obtained by heating a mixture of 4-aminodiphenylamine, quinol, and zinc chloride at 180°; a portion of the product can be purified by crystallisation, but the main portion, apparently in consequence of oxidation, must be reduced in alcoholic solution by zinc dust and glacial acetic acid before it is recrystallised. By treating its solution in boiling benzene with mercuric oxide, the substance is oxidised to 3-anilinoindophenol, $\text{O}:\text{C}_6\text{H}_4:\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NHPh}$, bluish-violet crystals containing 1 mol. CHCl_3 , m. p. 158°. C. S.

The Constitution of Capsaicin, the Pungent Principle of Capsicum. E. K. NELSON (*J. Amer. Chem. Soc.*, 1919, 41, 1115—1121).—The amount of capsaicin in cayenne pepper varies considerably, a very good sample yielding, when treated according to Micko's method (*A.*, 1899, i, 716; see also Nelson, *A.*, 1911, ii, 551), about 60 grams of the pure substance per 50 kilos.

The compound is now shown to be a condensation product of vanillylamine and a decenoic acid (annexed formula).



Capsaicin crystallises from a mixture of light petroleum and ether (9:1) in monoclinic plates (α , 1·520; β , 1·540; γ , 1·580), m. p. 65°. Its

methyl ether forms bundles of minute needles (α , 1·55; β , 1·58; γ , 1·60), m. p. 77—78°, and is only slightly pungent. On oxidation with alkaline permanganate, this ether yields veratric acid, and when hydrolysed by means of methyl-alcoholic hydrochloric acid, it gives 3:4-dimethoxybenzylamine hydrochloride, which crystallises in monoclinic rods or narrow plates (α , 1·505; β , 1·670; γ , 1·700) (compare Juliusberg, A., 1907, i, 219). Capsaicin itself yields 4-hydroxy-3-methoxybenzylamine hydrochloride (see below) when hydrolysed in the same way, but hydrolysis with 25% sodium hydroxide at 180° enables the acid fragment to be isolated in excellent yield. The alkaline liquid is saturated with carbon dioxide, extracted with ether to remove the decomposition products of the amine residue, the aqueous portion is then evaporated to dryness, the organic salt is separated by means of boiling alcohol, and finally decomposed by dilute sulphuric acid. The acid appears to be a new *decenoic acid*, $C_{10}H_{18}O_2$. It has m. p. -5°, b. p. 258—261°/atm. (corr.), forms a *dibromide*, m. p. 57—59°, and an *amide*, pearly leaflets, m. p. 96—97° (corr.), which differs from the amides of two decenoic acids described by Wallach, and the saturated *decoic acid* obtained by Paal's method has b. p. 260°, m. p. 24—25°, and immediately causes the liquefaction of decoic acid from coconut oil (compare Lapworth and Royle, T., 1919, 115, 1109).

The base, *vanillylamine* (4-hydroxy-3-methoxybenzylamine), was prepared for comparison by the reduction of vanillin oxime. It is very unstable, crystallises from water in slender needles, m. p. 131—133° (after drying at 110°), and yields a *hydrochloride*, colourless rods (α , 1·510; β , 1·705; γ , 1·735). J. C. W.

Solubility of Carbon Dioxide in Solutions of Chlorophyll.

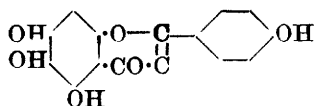
ROBERT KREMANN and NORBERT SCHNIDERSCHITSCH (*Monatsh.*, 1916, **37**, 659—679).—With the object of ascertaining whether chlorophyll and carbon dioxide form an additive compound in the assimilation of the latter by the leaves of trees, the authors have determined the solubility of carbon dioxide in 95% alcoholic solutions of chlorophyll both in the absence and the presence of light. The experiments were carried out both by the static method and the dynamic method. In the latter method, the amount of carbon dioxide dissolved was estimated by determinations of the electrical conductivity of the solutions. A similar series of experiments was also carried out with 95% alcohol which contained no chlorophyll. The experiments show that the solubility of carbon dioxide in alcohol and in alcoholic solutions of chlorophyll is practically the same. It must therefore be concluded that neither in the dark nor in daylight is there a measurable formation of an additive compound

between carbon dioxide and chlorophyll. Further, no such compound could be observed in a colloidal suspension of chlorophyll in 45% alcohol through which carbon dioxide had been bubbled. Consequently, if such an additive compound takes any part in the absorption of carbon dioxide by living leaves, this compound can only be present in an almost unrecognisable quantity. J. F. S.

The Tannin of the Knopper Gall. MAXIMILIAN NIERENSTEIN (T., 1919, 115, 1174—1180).

5 : 6 : 7-Trihydroxyflavone : Constitution of Scutellarein.

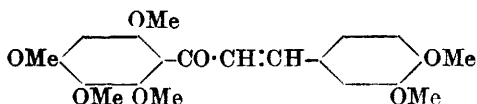
G. BARGELLINI (*Gazzetta*, 1919, 49, ii, 47—63).—The fact that scutellarein alone is obtained by the action of hydriodic acid on 2 : 3 : 4 : 6-tetramethoxyphenyl *p*-methoxybenzoylmethyl ketone, which thus undergoes demethylation and also loses 1 mol. of water, indicates that scutellarein is either 5:7:8:4'- or 5:6:7:4'-tetrahydroxyflavone (A., 1915, i, 84). The decision between these two constitutions is now made as follows. By condensation with methyl benzoate in presence of sodium, 2:3:4:6-tetramethoxyphenyl methyl ketone is converted into 2:3:4:6-tetramethoxyphenyl benzoylmethyl ketone, and hydrolysis of the latter by means of hydriodic acid, as above, yields a trihydroxyflavone, which may be either the 5:7:8- or the 5:6:7-derivative; as this compound is different from the 5:7:8-trihydroxyflavone (hydroxychrysin) described by Nierenstein (A., 1912, i, 292), it must be regarded as 5:6:7-trihydroxyflavone. On the assumption that the elimination of water in the formation of scutellarein from 2:3:4:6-tetramethoxyphenyl *p*-methoxybenzoylmethyl ketone takes place similarly to the elimination of water from benzoylmethyl 2:3:4:6-tetramethoxyphenyl ketone, scutellarein must be regarded as 5:6:7:4'-tetrahydroxyflavone (annexed formula).



Melting points different from those obtained by the author have been given by Nierenstein for certain of

these derivatives. Thus, for 2:3:4:6-tetramethoxyphenyl methyl ketone, the author finds m. p. 48—50°, and Nierenstein (T., 1917, 111, 4) 92—93°, and, in view of the ease with which *C*-methylated derivatives are formed when phloroglucinol and its derivatives, and also 1 : 2 : 3 : 5-tetrahydroxybenzene and its derivatives, are methylated, it may be that Nierenstein's so-called 2:3:4:6-tetramethoxyphenyl methyl ketone, prepared by direct methylation of the corresponding tetrahydroxy-compound, is in reality a *C*-methylated derivative.

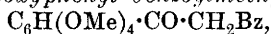
2:3:4:6:3':4'-Hexamethoxyphenyl styryl ketone (annexed formula), obtained by condensation of 2:3:4:6-tetramethoxyphenyl



methyl ketone with veratraldehyde, is a pale yellow compound, m. p. 127—128°, and dissolves in concentrated sulphuric acid with an intense red coloration.

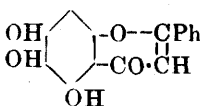
Nierenstein (*loc. cit.*) describes 2-hydroxy-3:4:6-trimethoxyphenyl methyl ketone, m. p. 125—126°, and 6-hydroxy-2:3:4-trimethoxyphenyl methyl ketone, m. p. 164—165°. The trimethylated derivative prepared by the author has m. p. 106—108°, and is probably the former of these compounds; its *acetyl* derivative, m. p. 106°, and its *benzoyl* derivative, m. p. 120—122°, have been prepared. With veratraldehyde in presence of sodium hydroxide, it yields 2-hydroxy-3:4:6:3':4'-pentamethoxyphenyl styryl ketone, m. p. 143°, as described by Nierenstein. The latter describes 2:6-dihydroxy-3:4-dimethoxyphenyl methyl ketone, m. p. 166—168°, whereas the dimethylated derivative obtained by the author has m. p. 162—163°; its *acetyl* derivative, m. p. 110—112°, has also been prepared. The tetra-, tri-, and di-methyl compounds all dissolve in concentrated sulphuric acid, giving a yellow coloration, changing to brownish-green and then to bluish-violet on heating; this colour reaction is probably common to all derivatives of 1:2:3:5-tetramethoxybenzene.

2:3:4:6-Tetramethoxyphenyl benzoylmethyl ketone,



forms yellow, prismatic crystals, m. p. 110—112°, and in alcoholic solution gives an intense red coloration with ferric chloride; a crystal of the compound is coloured red by concentrated sulphuric acid, the latter becoming yellow.

5:6:7-Trihydroxyflavone (annexed formula) forms a brownish-



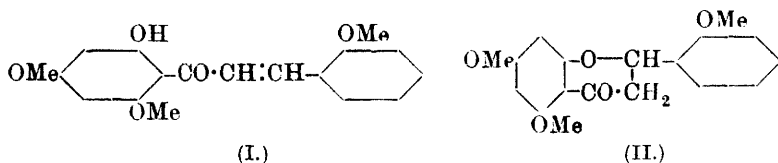
yellow powder, m. p. about 260° (decomp.), or, when prepared from the di- or tri-acetyl derivative, shining, yellow crystals, turning brown locally at 240—250°, m. p. 262—266°. It dissolves in aqueous borax to an intense yellow solution, in concentrated sulphuric acid to a yellow solution, in sodium hydroxide solution, giving a reddish-brown solution, and in sodium carbonate solution, giving a green solution turning brownish-red. Addition of a few drops of concentrated sulphuric acid to a hot solution of the compound in glacial acetic acid yields a red, crystalline compound similar to that given under these conditions by scutellarein. Addition of a little sodium amalgam to the alcoholic solution of the trihydroxyflavone results in the deposition of green flocks; scutellarein behaves similarly, whereas 5:7:4'-trihydroxyflavone (apigenin) and 6:7-dihydroxyflavone give red colorations, and 5:7:3':4':5'-pentahydroxyflavone reddish-brown flocks. Thus, the formation of green flocks with sodium amalgam is probably a reaction characteristic of flavones containing three vicinal hydroxyl groups in the benzopyrone nucleus, and may be of service as an indication of the constitution of other natural flavones or flavonols. The *diacetyl* derivative of 5:6:7-trihydroxyflavone, $\text{C}_{19}\text{H}_{14}\text{O}_7$, forms yellow needles, m. p. 198—200°, and gives a red coloration with ferric chloride in alcoholic solution. The *triacetyl* derivative, $\text{C}_{21}\text{H}_{16}\text{O}_8$, forms white needles, m. p. 190—192°, and dissolves in concentrated sulphuric acid to a yellow solution, but gives no coloration with ferric chloride in alcoholic solution. The (6:7-?) *dimethyl ether*,

$C_{17}H_{14}O_5$, forms yellow needles, m. p. 155—156°, and with ferric chloride in alcoholic solution gives a red coloration changing to green with excess of the reagent. The *trimethyl ether*, $C_{18}H_{16}O_5$, forms light, wool-like needles, m. p. 165—166°, and dissolves to a yellow solution in concentrated sulphuric acid, but gives no coloration with ferric chloride in alcoholic solution. T. H. P.

5:7:2'-Trihydroxyflavanol: Synthesis of Datiscetin.

G. BARGELLINI and E. PERATONER (*Gazzetta*, 1919, **49**, ii, 64—69). —5:7:2'-Trihydroxyflavanol has been prepared as follows. Condensation of 2-hydroxy-4:6-dimethoxyphenyl methyl ketone with the methyl ether of salicylaldehyde in presence of sodium hydroxide yields 2-hydroxy-4:6:2'-trimethoxyphenyl styryl ketone, which, when boiled with dilute hydrochloric acid in alcoholic solution, is converted partly into 5:7:2'-trimethoxyflavanone. Treatment with amyl nitrite transforms the latter into its *isonitroso*-derivative, and this, when heated with dilute sulphuric acid in acetic acid solution, gives 5:7:2'-trimethoxyflavanol. The latter should be identical with the trimethyl ether of the datiscetin of Marchlewski and Korczyński (*A.*, 1907, i, 435), and should yield datiscetin (5:7:2'-trihydroxyflavanol) when treated with hydriodic acid, but lack of material has prevented the completion of the work.

2-Hydroxy-4:6:2'-trimethoxyphenyl styryl ketone (I) forms

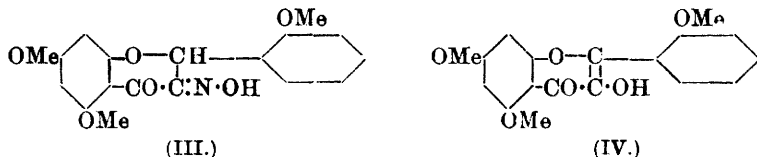


canary-yellow crystals, m. p. 106—108° and dissolves in concentrated sulphuric acid with an orange-red coloration.

5:7:2'-Trimethoxyflavanone (II) crystallises in white needles, m. p. 124—125°, and dissolves in concentrated sulphuric acid to a brownish-yellow solution.

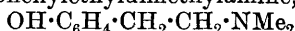
2-Oximino-5:7:2'-trimethoxyflavanone (III) forms pale yellow crystals, m. p. 189—190° (decomp.).

5:7:2'-Trimethoxyflavanol (IV) crystallises in pale yellow

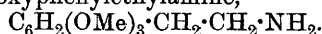


needles, m. p. 158—160°, and dissolves in concentrated sulphuric acid, giving a yellow solution which exhibits intense green fluorescence. Datiscetin also gives a fluorescent solution in sulphuric acid. T. H. P.

The Anhalonium [Cactus] Alkaloids. I. Anhaline and Mezcaline. ERNST SPÄTH (*Monatsh.*, 1919, 40, 129—154).—The cactus alkaloids have been investigated most completely so far by Heffter (A., 1895, i, 120; 1896, i, 267; 1898, i, 499; 1901, i, 736; 1905, i, 877), and seven bases are described in the literature, namely, anhaline, mezcaline, pellotine, anhalonidine, anhalonine, anhalamine, and lophophorine. These have about the same physiological properties (Mogilewa, *Arch. expt. Path. Pharmak.*, 1903, 49, 137) and are closely related chemically. It is now shown that anhaline is identical with the hordenine of barley germs, that is, it is β -*p*-hydroxyphenylethyldimethylamine,

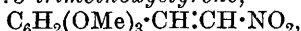


(Léger, A., 1906, i, 204, 761; Rosenmund, A., 1910, i, 241), and mezcaline has been synthesised by a method which shows that it is β -3:4:5-trimethoxyphenylethylamine,

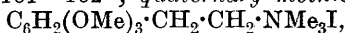


Anhalonine and lophophorine each contain a methoxy-group and two non-hydroxylic oxygen atoms, but the other bases are simply methylated members of the 3:4:5-trihydroxyphenylethylamine series.

Synthesis of Mezcaline.—Gallic acid is methylated by means of methyl sulphate, and then converted into 3:4:5-trimethoxybenzoyl chloride by the action of phosphorus pentachloride. This is reduced in boiling toluene by hydrogen in the presence of palladinised barium sulphate, the yield of 3:4:5-trimethoxybenzaldehyde being good, although some by-products are formed (Rosenmund, A., 1918, i, 300). The aldehyde is condensed with nitromethane to form ω -nitro-3:4:5-trimethoxystyrene,



long, yellow needles, m. p. 120—121°, and this is reduced by means of zinc dust and acetic acid to an oxime, and then by sodium amalgam to β -3:4:5-trimethoxyphenylethylamine, which is a colourless, highly refractive, viscous oil having b. p. 180—180.5°/12 mm. and a faint, basic odour. The procedure at all these stages is that devised by Rosenmund (A., 1910, i, 110). The base gives the following derivatives, which are identical with those obtained from a specimen of Merck's mezcaline, and already described in part by Heffter; *sulphate*, $\text{B}_2\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$, long, glistening prisms, m. p. 183—186°; *picrate*, yellow crystals, m. p. 216—218°; *platinichloride*, rosettes of straw-yellow needles, m. p. 187—188°; *aurichloride*, $\text{B} \cdot \text{HAuCl}_4 \cdot \text{H}_2\text{O}$, orange needles, decomp. 140—141°; *benzoyl derivative*, m. p. 120—121°; *m-nitrobenzoyl derivative*, m. p. 161—162°; *quaternary methiodide*,



m. p. 224—225°.

Heffter found on analysis that mezcaline behaves as though it contains a methylamino-group, $-\text{NHMe}$, and this is confirmed. The explanation seems to be that some rearrangement in the molecule proceeds during the analysis, for Heffter himself disposed of the alternative formula, $\text{C}_6\text{H}_2(\text{OMe})_3 \cdot \text{CH}_2 \cdot \text{NHMe}$. Still another alternative, $\text{C}_6\text{H}_2(\text{OMe})_3 \cdot \text{CHMe} \cdot \text{NH}_2$, is now negatived by the

synthesis of the base with this formula. 3:4:5-Trimethoxyphenyl methyl ketone (Mauthner, A., 1910, i, 680) is converted into the *oxime*, needles, m. p. 102—103°, and this is reduced by means of sodium amalgam. α -3:4:5-Trimethoxyphenylethylamine is a strong base which forms a solid carbonate on exposure to the air. Its *benzoyl* derivative has m. p. 150—151°, and the *quaternary methiodide*, $C_6H_2(OMe)_3 \cdot CHMe \cdot NMe_3I$, melts at 180—182°, then resolidifies, melts again at 235—237°, and decomposes at 250—255°.

J. C. W.

Some Cases of Solubility Influence. II. Compounds of Caffeine existing in Aqueous Solution. G. BARGELLINI (*Gazzetta*, 1919, 49, i, 191—200).—Cryoscopic investigation of solutions containing caffeine, together with either antipyrine, sodium benzoate, resorcinol, quinol, or catechol gives results indicating the formation of compounds between the solutes, the solubility of the caffeine being apparently increased. With phloroglucinol or pyrogallol, however, caffeine appears to form compounds exhibiting but slight solubilities in water (compare Ultée, A., 1910, i, 132). The solubility of caffeine in water is about 1%, in 10% resorcinol solution about 3%, and in more concentrated resorcinol solutions still more.

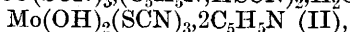
T. H. P.

Compound of Yohimbine containing Arsenic. W. GRÜTTEFIEN (U.S. Pat. 1305462).—Arsenic acid (150·7 parts) and yohimbine (368 parts) are dissolved in water (1000 parts). The solution is filtered and evaporated, the residue is mixed with acetone, and the salt thus obtained is filtered and dried at 100°. *Yohimbine arsenate* thus produced forms an almost colourless powder, m. p. 243°. *Yohimbine methylarsinate*, m. p. 203°, is obtained from methylarsinic acid (130 parts) and yohimbine (368 parts). *Yohimbine phenylarsinate*, m. p. about 140°, is produced by the interaction of phenylarsinic acid (202 parts) and yohimbine (368 parts) dissolved in alcohol (1000 parts). *Yohimbine chloroarsenobehenolate* is a faintly coloured powder, m. p. about 90°, soluble in water, alcohol, and acetone. It is produced from chloroarsenobehenolic acid (462·5 parts) and yohimbine (368 parts) dissolved in acetone (10,000—15,000 parts). If necessary, the solution is filtered and the filtrate carefully evaporated. The viscous paste which is at first obtained becomes solid after keeping for a short time in a desiccator, and can then be easily pulverised. These compounds are stated to be especially suitable as therapeutic agents because they do not possess the pronounced irritating effect on the intestine which is common both to arsenic compounds generally and to yohimbine.

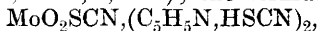
CHEMICAL ABSTRACTS.

Colour Reactions of Molybdenum and Tungsten. I. G. A. BARBIERI (*Atti R. Accad. Lincei*, 1919, [v], 28, i, 351—355).—According to Sand and Burger (A., 1905, i, 923; 1906, i, 487), and Rosenheim and Koss (A., 1906, i, 603), the action of pyridine on the red and violet liquids obtained from an acidified solution

containing a molybdate and a thiocyanate, either by boiling or by treating in the cold with zinc, tin, or other reducing agent, yields the compounds $\text{MoO}(\text{SCN})_3 \cdot (\text{C}_5\text{H}_5\text{N} \cdot \text{HSCN})_2 \cdot \text{H}_2\text{O}$ (I) and

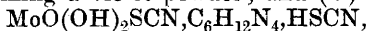


the molybdenum being quinquevalent. Since compound II is formed in acid solution, it is more probable that the pyridine unites with the thiocyanic acid, and that the molybdenum exists as molybdyl, MoO_2 (A., 1916, i, 627); the formula,



for this compound would explain also its conversion into compound I by treatment with thiocyanic acid.

When molybdic acid is reduced in presence of thiocyanic acid (Braun's reaction, *Zeitsch. anal. Chem.*, 1863, **2**, 36), the colorations produced may be due partly to sexa- and partly to quinquevalent molybdenum. The latter alone is present in molybdenyl ammonium chloride, $\text{MoOCl}_3 \cdot 2\text{NH}_4\text{Cl}$, which gives an orange-red coloration when treated, in a solution acidified with hydrochloric acid, with excess of ammonium thiocyanate; the colour changes to blood-red and then to violet on dilution or heating, further addition of water producing in succession orange-yellow and yellow colorations, and finally decolorisation. The different colours are hence the result of hydrolysis. The orange-yellow liquid gives with pyridine thiocyanate the compound I (above), whilst treatment of the coloured solutions with a hexamethylenetetramine salt under definite experimental conditions gives the compounds: (III) $\text{Mo}(\text{OH})_2(\text{SCN})_3 \cdot \text{C}_6\text{H}_{12}\text{N}_4 \cdot \text{HSCN} \cdot 2\text{H}_2\text{O}$, black, prismatic crystals; (IV) $\text{Mo}(\text{OH})_3(\text{SCN})_2 \cdot \text{C}_6\text{H}_{12}\text{N}_4 \cdot \text{HSCN} \cdot 2\text{H}_2\text{O}$, blackish-green crystals forming a violet powder; and (V)



orange-yellow prisms. Compounds III and IV give violet alcoholic solutions which become orange-yellow when diluted with water and heated, and, on cooling, then deposit compound V; treatment of the latter with thiocyanic acid yields a violet solution.

T. H. P.

Synthetic Investigations in the Quinine Series. I. Synthesis of β -Collidine [4-Methyl-3-ethylpyridine]. L.

RUZICKA and V. FORNASIR (*Helv. Chim. Acta*, 1919, **2**, 338—348).

—The authors have succeeded in synthesising β -collidine [4-methyl-3-ethylpyridine], the various steps in the process being as follows:

(1) Preparation of 2:6-dihydroxy- β -collidine, either by heating γ -cyano- β -methyl- α -ethylglutaconimide (5-cyano-2:6-dihydroxy-4-methyl-3-ethylpyridine) (compare Guareschi, A., 1897, i, 168) with hydrobromic acid, or by condensing ethyl ethylacetoacetate with ethyl cyanoacetate in presence of sodium and treating the cyano-glutaconic ester thus obtained with sodium hydroxide (compare Rogerson and Thorpe, T., 1905, **87**, 1685); (2) conversion of the 2:6-dihydroxy- β -collidine into 2:6-dichloro- β -collidine by means of phosphoryl chloride; and (3) removal of the chlorine atoms by treatment with hydriodic acid, monochloro- β -collidine, and then β -collidine, being formed.

γ -Cyano- β -methyl- α -ethylglutaconimide has m. p. about 220° (crude) (Guareschi, *loc. cit.*, gave 234°), and its ammonium derivative, m. p. about 315° (Guareschi gave m. p. about 300°).

2:6-Dichloro-4-methyl-3-ethylpyridine, $N \begin{smallmatrix} \text{CCl} \cdot \text{CEt} \\ \text{CCl} \cdot \text{CH} \end{smallmatrix} > \text{CMe}$, is a colourless, mobile oil, b. p. 140°/12 mm., having a piercing odour and an inflammatory action on the skin.

2-Chloro-4-methyl-3-ethylpyridine, $N \begin{smallmatrix} \text{CCl} \cdot \text{CEt} \\ \text{CH} = \text{CH} \end{smallmatrix} > \text{CMe}$, forms a colourless, mobile oil with the odour of pyridine, b. p. 110°/12 mm. Its *picrate* has m. p. about 110°. T. H. P.

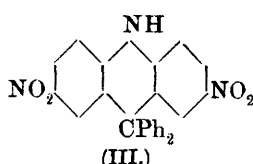
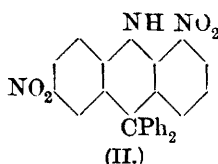
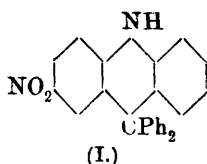
Compounds of 2-Phenylquinoline-4-carboxylic Acid with Halogen Acids. H. W. RHODEHAMEL (U.S. Pat. 1306439).—Compounds of 2-phenylquinoline-4-carboxylic acid with halogen acids are prepared by mixing the parent materials, using an excess of halogen acid, and then removing the excess of the latter by drying. The *hydriodide* forms orange-yellow crystals, m. p. 243°. It is useful as a therapeutic agent for rheumatism and gout. The *hydrobromide* forms brownish-yellow crystals, m. p. 255°. The *hydrochloride*, m. p. 223°, and *hydrofluoride* form lemon-yellow crystals. CHEMICAL ABSTRACTS.

Nitro-derivatives of 5-Diphenyldihydroacridine. F. KEHRMANN, HENRI GOLDSTEIN, and PETER TSCHUDI (*Helv. Chim. Acta*, 1919, **2**, 315—323. Compare A., 1918, i, 311; ii, 344).—In presence of acids, 5-diphenyldihydroacridine (compare Baeyer and Villiger, A., 1904, i, 898) is readily oxidised at the ordinary temperature by various oxidising agents, yielding coloured products with the characters of salts; the study of these products is attended with considerable difficulty. By nitric acid diluted largely with glacial acetic acid, 5-diphenyldihydroacridine is energetically attacked, with formation of crystalline nitro-derivatives, of which six have been isolated pure (see below). The corresponding amino-derivatives behave towards oxidising agents like the leuco-compounds of colouring matters, showing the characteristic properties of quinoneimide dyes and resembling particularly many azoxine dyes. The behaviour of the nitro-derivatives towards alcoholic alkali hydroxide accords with the assumption that at least one nitro-group occupies the para-position with respect to the ter-valent ring nitrogen atom; they dissolve in the alkali, yielding pronounced green, red, and blue colorations, thus resembling closely the analogous nitro-derivatives of phenazoxine and thiodiphenylamine.

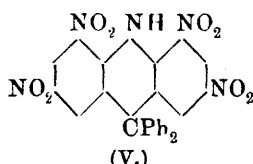
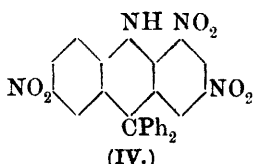
The *mononitro*-derivative of 5-diphenyldihydroacridine (I) forms compact, many-faced crystals with the colour of crystalline potassium dichromate, or, when ground, a pale orange powder, m. p. 300—301°; concentrated sulphuric acid dissolves and decomposes it, with formation of a deep blue coloration. Its *acetyl* derivative forms large, four-sided plates, m. p. 215°, yielding an

almost white powder. Addition of alkali hydroxide solution to the hot alcoholic solution yields a dichroic liquid, which is greenish-yellow in thin and purple-red in thick layers.

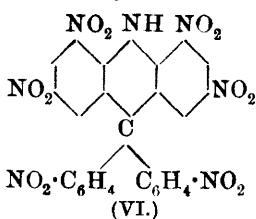
The *dinitro*-derivative A (formula II), forms heavy, orange-



yellow, many-faced crystals, m. p. 287—288°, giving a golden-yellow powder; its solution in alcoholic sodium hydroxide is greenish-yellow in thin and violet-brown in thick layers. The *dinitro*-derivative B (formula III) forms compact, lemon-yellow crystals with a slight blue reflex and a yellow powder with a green tinge; it begins to decompose at about 300° and has m. p. about 322·5°. Its alcoholic alkali hydroxide solution is blue in thin and deep purple in thick layers.



The *trinitro*-derivative (formula IV) forms orange-yellow leaflets containing benzene of crystallisation and a golden-yellow powder,



m. p. 257—258°; its solution in alcoholic alkali hydroxide is magenta-red, and becomes reddish-violet on addition of a little water, whilst much water forms a yellow, flocculent precipitate.

The *tetranitro*-derivative (formula V) forms pale orange-yellow needles and a pale yellow powder, m. p. about 180°; in alcoholic alkali hydroxide it gives a magenta-red solution, changing to violet on dilution.

The *hexanitro*-derivative (formula VI) forms granular, yellow crystals, m. p. 317—318° (decomp.), and dissolves in alcoholic alkali hydroxide to a magenta-red liquid, the colour of which is unchanged by dilution.

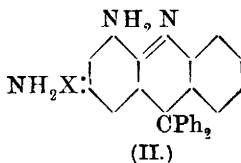
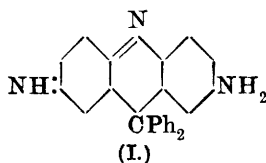
T. H. P.

Carbazine Dyes, a New Class of Quinone-imide Derivatives. F. KEHRMANN, HENRI GOLDSTEIN, and PETER TSCHUDI (*Helv. Chim. Acta*, 1919, 2, 379—397).—The amines obtained by reduction of the nitro-derivatives prepared from 5-diphenyldi-hydroacridine (preceding abstract) behave as the leuco-compounds of dyes into which they are transformed by oxidation. Owing to their evident analogy to azoxine and thiazine dyes, the name

carbazine is given to these dyes. Despite their relation to acridine, carbazine dyes exhibit little similarity to the acridine dyes, the dissimilarity being sufficiently explained by the difference between the chromophores in the two cases. Like the azine, azoxine, and thiazine dyes, carbazine dyes are derivatives of quinone-di-imide, this relationship being fully borne out by their properties.

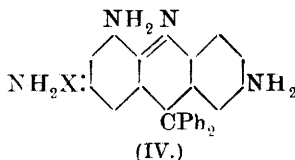
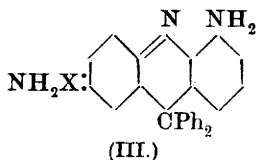
The introduction of an amino-group is accompanied by the following colour changes in the mono-acid salts: with carbazine [dihydroacridine], from yellow to bluish-green; with azoxine, from yellowish-red to bluish-violet; with thiazine, from violet-red to violet-blue, and with safranine, from violet-red to scarlet. The absolute value of the bathochromic or hypsochromic effect produced by the introduction of an amino-group into a chromogen is in general a function of the basicity of the complex it enters, the action being the more strongly bathochromic the less this basicity is developed. Thus, to explain the conversion of the bluish-green malachite-green into the bluish-violet crystal-violet by the introduction of a second *p*-dimethylamino-group, the hypothesis of colours of the second order is unnecessary. Indeed, whether the introduction of amino-groups into coloured complexes produces deepening of the colour or the reverse depends primarily on the chemical nature of the complex and secondarily on the positions assumed by the entering groups.

The quinone-imide base (formula I), corresponding with the



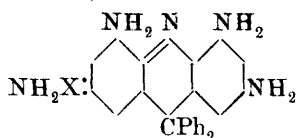
bluish-green mono-acid salts mentioned above, is yellowish-red in ethereal solution and shows a pronounced yellow fluorescence; even ammonium carbonate separates it completely from its salts. Oxidation by means of ferric chloride of the colourless leuco-diamine prepared by reduction of the yellowish-red dinitro-compound (*loc. cit.*) yields a dye (formula II or III), which, as mono-acid salt, is deep olive-green; the corresponding dark cherry-red base is even weaker than the preceding, as its salts are decomposed by sodium acetate.

Reduction of the trinitro-compound (*loc. cit.*) yields a colourless leuco-triamine, which is oxidised by ferric chloride to a colouring matter (formula IV) with an intense, pure violet mono-acid

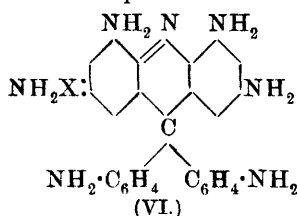


salt; the base, which is separated from its salts by ammonia, but only incompletely by ammonium carbonate, is deep orange-red, but non-fluorescent in ethereal solution. Hence the first amino-group exerts a bathochromic, but the second a hypsochromic, influence, with the limitation that the colour strength is considerably increased. Comparative dyeing tests with tannin-mordanted cotton show that the colour strength increases from the chromogen to the violet diamine, and then gradually falls until the pentamine is reached.

The leuco-tetramine gives on oxidation a pure blue mono-acid salt of the probable formula V, and the hexamine one of the probable formula VI, also blue. With both salts correspond imide bases,



(V.)

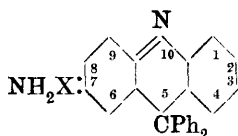


(VI.)

which are liberated from their salts only by the strongest inorganic bases, that derived from the hexamine only incompletely; boiled distilled water extracts the blue hydrates quantitatively from the violet-red ethereal solutions.

By excess of more or less concentrated acids, all the colouring matters are converted into poly-acid salts of different colour, these being mostly hydrolysed with ease by water.

7-Amino-5-diphenylacridine salts (annexed formula) are obtained



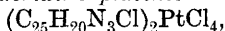
by oxidation of the leuco-compound, 7-amino-5-diphenyldihydroacridine, in acid solution by means of ferric chloride. Other solid salts are difficult to obtain, but the *perchlorate*, $C_{25}H_{19}N_3ClO_4$, forms a pure yellow, pulverulent, crystalline precipitate

exploding when heated.

5-Diphenylacridine, $C_{25}H_{18}N_2$, forms small, pale yellow crystals decomposing without melting at 160° , and acts as a very weak base.

1(or 9):7-Diaminodiphenylacridine hydrochloride, $C_{25}H_{20}N_3Cl$, forms deep, olive-green, crystalline flocks, and the *platinichloride*, $(C_{25}H_{20}N_3Cl)_2PtCl_4$, small, dark green crystals. The *imide* base, $C_{25}H_{19}N_3$, separates, apparently as a hydrate, in deep red flocks, changing in a few minutes to fine crystals.

3:7-Diaminodiphenylacridine platinichloride,



forms metallic-green crystals, somewhat soluble in water to a greenish-blue solution. The *chloride* forms metallic-green crystals with the lustre of brass. The *imide* base, $C_{25}H_{19}N_3$, forms copper-red crystals with a golden lustre, m. p. $240-250^\circ$ (decomp.).

3:7:9-Triaminodiphenylacridine chloride, $C_{25}H_{21}N_4Cl$, forms

compact crystals with a coppery lustre, and the *platinichloride*, microscopic, blackish-violet crystals insoluble in water.

1 : 3 : 7 : 9-*Tetra-aminodiphenylacridine chloride*, $C_{25}H_{22}N_5Cl$, forms needles with a coppery lustre, and the *base*, leaflets with the lustre of bronze.

Hexa-aminodiphenylacridine chloride (formula VI), $C_{25}H_{24}N_7Cl$ forms almost black prisms with a slight metallic lustre. The base exhibits highly basic characters, and was not isolated, as it is not completely liberated from its salts by alkali hydroxide, and even in ethereal solution rapidly absorbs carbon dioxide from the air.

The constitution of these colouring matters is discussed.

T. H. P.

Derivatives of 3:5-Dinitrophenoxazine. EMIL MISSLIN and ADOLF BAU (*Helv. Chim. Acta*, 1919, **2**, 285—315).—The objects of this investigation were: (1) to ascertain how far substitution in *o*-aminophenol by the radicles NO_2 , Cl , and $NHAc$ may be carried without preventing the formation of phenoxazines by the action of either picryl chloride or the more readily accessible 2:4:6-trinitroanisole in presence of an alkaline medium, and (2) to determine if in all cases the formation of phenoxazine takes place by way of an intermediate diphenylamine derivative, or if in certain cases the initial formation of a diphenyl ether is to be assumed.

The results obtained show that the action either of 2:4:6-trinitroanisole or of picryl chloride on *o*-aminophenol or its nitro-, chloro-, bromo-, or acetyl-amino-substituted derivatives of the type of picramic acid leads in presence of alkali to the formation of derivatives of 3:5-dinitrophenoxazine, diphenylamine compounds being formed as intermediate products. It is highly probable, also, that other substituted *o*-aminophenols containing the groups named, with the exception of those in which the substitution occurs in the ortho-position to the amino-group, react in the same sense with 2:4:6-trinitroanisole or picryl chloride. When suspended in alcohol, 3:5-dinitrophenoxazines substituted in the 7-position by NO_2 , Cl , Br , or $NHAc$ yield Bordeaux-red or violet colorations on addition of alkali hydroxide, whilst 3:5-dinitrophenoxazines with a nitro-group in the 6-position yield a pure blue coloration under these conditions. With simultaneous substitution in the 6- and 7-positions, the coloration is determined by the more highly negative substituent, or, if the two substituents are of similar character, by that in the 6-position. The condensation product obtained in the cold from picryl chloride and the potassium derivative of *o*-acetylaminophenol yields Turpin's 3:5-dinitrophenoxazine (T., 1891. **59**, 714) on treatment with alkali.

3:5-Dinitrophenoxazine, formed from 2:4:6-trinitroanisole and *o*-aminophenol in alcoholic solution in presence of potassium hydroxide, is also obtained from the *p*-toluenesulphonic ester of 2:4:6-trinitro-2'-hydroxydiphenylamine under similar conditions, and from 2:4:6-trinitro-2'-hydroxy-*N*-acetyldiphenylamine by treatment with ammonia in alcoholic solution.

8-Chloro-3:5-dinitrophenoxazine, $C_{12}H_6O_5N_3Cl$, formed either

from 2:4:6-trinitroanisole and 4-chloro-2-aminophenol or from 5'-chloro-2:4:6-trinitro-2'-hydroxydiphenylamine *p*-toluenesulphonate, crystallises in brick-red or deep brownish-red needles. In concentrated sulphuric acid it forms a Bordeaux-red solution, which precipitates it unchanged on dilution; when suspended in alcohol, it yields a pure violet coloration with alkali hydroxide.

3:5:8-*Trinitrophenoxazine*, $C_{12}H_6O_7N_4$, obtained from 2:4:6-nitroanisole and 4-nitro-2-aminophenol, forms deep reddish-brown needles, and gives a Bordeaux-red solution in alkaline alcohol.

3:5-*Dinitro-8-acetylaminophenoxazine*, $C_{14}H_{10}O_6N_4$, prepared from 4-acetyl-amino-2-aminophenol and potassium 3:5-dinitro-4:4'-dimethoxyquinolnitrolate (compare Meisenheimer, A., 1902, i, 795), forms dark brown, velvety, felted needles. Its solution in concentrated sulphuric acid is first brownish-red and then dark red, addition of water producing a brownish-yellow precipitate. Its suspension in alcohol is coloured violet by potassium hydroxide.

3:5:9-*Trinitrophenoxazine*, obtained from 2:4:6-trinitroanisole and 5-nitro-2-aminophenol, was prepared by Kehrmann and Saager (A., 1903, i, 279) by nitration of 3:5-dinitrophenoxazine.

8-*Chloro-3:5-dinitro-10-aminophenoxazine*, $C_{12}H_7O_5N_4Cl$, obtained from 4-chloro-2:6-diaminophenol and 2:4:6-trinitroanisole, forms slender, reddish-brown, shining needles, gives a yellowish-brown solution in concentrated sulphuric acid, and yields a dull violet coloration with potassium hydroxide in alcohol.

8:10-*Dichloro-3:5-dinitrophenoxazine*, $C_{12}H_5O_5N_3Cl_2$, prepared from 4:6-dichloro-2-aminophenol and 2:4:6-trinitroanisole, forms small, reddish-brown, shining crystals, sparingly soluble in concentrated sulphuric acid, giving a reddish-violet coloration; in alkaline alcohol it forms a violet solution with a red tinge.

8:10-*Dibromo-3:5-dinitrophenoxazine*, $C_{12}H_5O_5N_3Br_2$, prepared like the corresponding dichloro-compound, forms deep reddish-brown, shining needles, and dissolves slightly in concentrated sulphuric acid with a faint blue coloration; with alcoholic alkali, a violet coloration with a red tinge is formed.

8-*Chloro-3:5:10-trinitrophenoxazine*, $C_{12}H_5O_7N_4Cl$, obtained from 2:4:6-trinitroanisole and 4-chloro-6-nitro-2-aminophenol, crystallises in drusy masses of matt, light brown leaflets, and gives a brownish-orange solution in concentrated sulphuric acid; its suspension in alcohol gives a violet coloration with alkali hydroxide.

3:5:8-*Trinitro-10-aminophenoxazine*, $C_{12}H_7O_7N_5$, prepared from 4-nitro-2:6-diaminophenol and potassium 3:5-dinitro-4:4'-dimethoxyquinolnitrolate (compare Meisenheimer, *loc. cit.*), crystallises in shining, reddish-brown to garnet-red needles, and dissolves readily in concentrated sulphuric acid to an intense brownish-yellow solution. In alcoholic potassium hydroxide, it dissolves incompletely to a dirty, brownish-red solution. When boiled with acetic anhydride and fused sodium acetate, it is converted into 3:5:8-*trinitro-10-acetylaminophenoxazine*, $C_{14}H_9O_8N_5$, which may also be obtained from 4-nitro-6-acetyl-amino-2-aminophenol and potassium 3:5-dinitro-4:4'-dimethoxyquinolnitrolate (compare Meisenheimer, *loc. cit.*), and which forms brownish-yellow leaflets

with the lustre of gold. It dissolves easily in concentrated sulphuric acid to an orange-yellow solution, and partly in alcoholic alkali hydroxide with a violet coloration showing a red tinge.

10-Chloro-3:5:8-trinitrophenoxazine, $C_{12}H_5O_7N_4Cl$, prepared from 2:4:6-trinitroanisole and 6-chloro-4-nitro-2-aminophenol, forms drusy masses of small, reddish-brown, shining crystals, and readily gives an orange solution in concentrated sulphuric acid; with alcohol and potassium hydroxide, it gives a reddish-violet to Bordeaux-red solution.

3:5:10-Trinitro-8-acetylaminophenoxazine, $C_{14}H_9O_8N_5$, obtained from 4-acetyl-amino-6-nitro-2-aminophenol and potassium 3:5-dinitro-4:4'-dimethoxyquinolnitrolate, forms shining, flat, pale reddish-brown needles, and gives a brownish-orange solution in concentrated sulphuric acid and a violet coloration with alkali hydroxide in suspension in alcohol.

8-Chloro-3:5:9-trinitrophenoxazine, $C_{12}H_5O_7N_4Cl$, obtained either from 2:4:6-trinitroanisole and 4-chloro-5-nitro-2-aminophenol or by nitration of 8-chloro-3:5-dinitrophenoxazine, crystallises in stellar aggregates of shining, garnet-red needles, and gives a dirty, bluish-red solution in concentrated sulphuric acid and a pure blue coloration with alkali hydroxide and alcohol.

3:5:7:9-Tetranitrophenoxazine, obtained by nitration of 3:5:9-trinitrophenoxazine, agrees in properties with Kehrman and Saager's preparation (*loc. cit.*).

3:5:9-Trinitro-8-methylphenoxazine, $C_{13}H_8O_7N_4$, prepared from 2:4:6-trinitroanisole and 5-nitro-2-amino-*p*-cresol, forms deep reddish-brown, shining needles, and readily dissolves in concentrated sulphuric acid to a dirty, brownish-red solution; a pure blue solution is obtained in alcohol and potassium hydroxide.

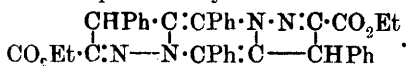
3:5:8:10-Tetranitrophenoxazine, $C_{12}H_5O_9N_5$, prepared from picramic acid and either 2:4:6-trinitroanisole or picryl chloride, forms dark brown or steel-blue needles, and yields an intensely golden-yellow solution in concentrated sulphuric acid and a bluish-red solution in alcoholic alkali hydroxide.

3:5:8:9-Tetranitrophenoxazine, $C_{12}H_5O_9N_5$, prepared by nitrating 3:5:8-trinitrophenoxazine, forms long, reddish-brown leaflets with a green, metallic lustre, containing acetic acid of crystallisation, and assumes an orange-red colour when dried. It dissolves easily in concentrated sulphuric acid with an orange-red coloration, and in alcohol containing alkali hydroxide to a greenish-blue solution.

T. H. P.

Coloured Condensation Products from Ketonic Pyrazoline Derivatives. E. P. KOHLER and L. L. STERLE (*J. Amer. Chem. Soc.*, 1919, **41**, 1105—1108).—The ketopyrazolines having the structure $-CO\cdot CH < \begin{smallmatrix} \diagup \\ NH- \end{smallmatrix}$ give highly fluorescent solutions in alcohol containing a trace of hydrogen chloride. Some of the products have now been isolated. They are very sparingly soluble substances of high m. p. and molecular weight, and outwardly resemble the most brilliant rhodamine dyes.

Hydrogen chloride is passed into a suspension of ethyl 5-benzoyl-4-phenylpyrazoline-3-carboxylate (this vol., i., 531) in boiling methyl alcohol, and the crimson precipitate is collected as soon as the ester has disappeared and boiled for some time with carbon disulphide. The compound, $C_{38}H_{32}O_4N_4$, is thereby changed into a mass of stout needles, m. p. 266—268°, which sublime freely at above 400° in a vacuum. It is very slightly soluble in benzene, the solution appearing a brilliant crimson-orange by reflected light and purple by transmitted light. On continuing the action of hydrogen chloride, the substance takes up water and the acid to form a yellow compound, $C_{38}H_{35}O_5N_4Cl$, plates, m. p. 258—259°, and when boiled with acetic acid for some time it combines with $2H_2O$ to give the colourless compound, $C_{38}H_{36}O_6N_4$, needles, m. p. 181°. From an approximate determination of its molecular weight, it appears that the compound may have the formula



Ethyl 5-*p*-bromobenzoyl-4-phenylpyrazoline-3-carboxylate (*ibid.*) gives a similar product, $C_{38}H_{31}O_4N_4Br$, purple-red needles, m. p. 268—270°.

Distyryl ketone reacts with ethyl diazoacetate in light petroleum at 50—70° to give ethyl 5-cinnamoyl-4-phenylpyrazoline-3-carboxylate, $CHPh \cdot CH \cdot CO \cdot CH < \begin{array}{c} CHPh \cdot C \cdot CO_2Et \\ | \quad | \\ NH \quad N \end{array}$, pale yellow plates, m. p. 164·5—165°, solutions of which become blood-red with hydrogen chloride. Styryl methyl ketone yields ethyl 5-acetyl-4-phenylpyrazoline-3-carboxylate, white needles, m. p. 127°, solutions of which give an orange colour with hydrochloric acid.

Ethyl 5-acetyl-4-phenylpyrazoline-3:5-dicarboxylate, m. p. 76°, was obtained by Buchner. The present authors have obtained an isomeride with m. p. 105—106°. This gives no colour with alcoholic hydrogen chloride. J. C. W.

Asymmetric Dyes. C. W. PORTER and C. T. HIRST (*J. Amer. Chem. Soc.*, 1919, **41**, 1264—1267).—A number of dyes containing an asymmetric carbon atom have been prepared with the idea of contributing to the knowledge of vital stains, and one has been discovered on which wool acts selectively, absorbing more of the lævo- than the dextro-modification.

The parent substance is *p*-aminobenzophenone, obtained by condensing benzoyl chloride with phthalanilide in the presence of zinc chloride. This is converted into *p*-aminobenzhydrol by reduction, and into carbinols by the Grignard reaction, and these bases, containing an asymmetric carbon atom, are diazotised and coupled with (a) β -naphthol, giving dyes which are insoluble in acids, alkalis, or water, (b) dimethylaniline in the presence of about 0·1*N*-hydrochloric acid, and (c) naphtholsulphonic acids and naphthylaminesulphonic acids, to give soluble dyes.

p-Aminodiphenylmethylcarbinol, $OH \cdot CMePh \cdot C_6H_4 \cdot NH_2$, has m. p. 101°, and *p*-aminodiphenylethylcarbinol forms colourless

plates, m. p. 103°. The *dyes* mentioned in tabular form in the original are as follows: $\text{OH}\cdot\text{CHPh}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$, red, m. p. 169·5°; $\text{OH}\cdot\text{CMePh}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$, red, m. p. 190°;

$\text{OH}\cdot\text{CEtPh}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$,
crimson, m. p. 149°; $\text{OH}\cdot\text{CHPh}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$, red, m. p. 145°; $\text{OH}\cdot\text{CMePh}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$, yellow, m. p. 177°; $\text{OH}\cdot\text{CEtPh}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$, orange, m. p. 138—139°; $\text{OH}\cdot\text{CHPh}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_4(\text{SO}_3\text{H})_2\cdot\text{OH}$, red, m. p. 162°;
 $\text{OH}\cdot\text{CEtPh}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_5(\text{OH})\cdot\text{SO}_3\text{H}$,
dark red, m. p. 120—122°; $\text{OH}\cdot\text{CMePh}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_5(\text{OH})\cdot\text{SO}_3\text{H}$,
red, m. p. 150—152°. J. C. W.

The Constitution of Internal Diazo-oxides (Diazo-phenols).

II. GILBERT T. MORGAN and ERIC DODDRELL EVANS (T., 1919, 115, 1126—1140).

Action of Phenylhydrazine on Phthalaldehydic and Phthalonic Acids: Phenyl-hydrazo- and Azo-phthalide. PRAFULLA CHANDRA MITTER and JNANENDRA NATH SEN (T., 1919, 115, 1145—1148).

Researches on Proteins. VI. The Destructive Distillation of Fibroin. TREAT B. JOHNSON and PETER G. DASCHAVSKY (*J. Amer. Chem. Soc.*, 1919, 41, 1147—1149).—Like Pictet and Cramer (this vol., i, 227), the authors have also commenced a study of the destructive distillation of proteins, choosing in the first instance silk fibroin, because it contains no sulphur and because its chief amino-acids are well known and few in number (glycine 33%, alanine 16%, and tyrosine 10%). Distilling quantities of about 1600 grams at a time, under 25—27 mm., the authors obtain about 16% of volatile and gaseous products, soluble in sodium hydroxide or sulphuric acid, 41% of coke, and 43% of a red oil which certainly contains phenol. J. C. W.

Application of the Kjeldahl Method to Compounds of Brucine, with Reference to the Brucine Salt of a New Nucleotide. WALTER JONES (*J. Pharm. Exp. Ther.*, 1919, 14, 489—493).—The Kjeldahl method gives exact results with salts of brucine. This fact has been applied in determining the nature of the brucine salt of a nucleotide obtained by partial oxidation of yeast-nucleic acid with potassium permanganate. J. C. D.

Action of Enzymes on Starches of Different Origin. H. C. SHERMAN, FLORENCE WALKER, and MARY L. CALDWELL (*J. Amer. Chem. Soc.*, 1919, 41, 1123—1129).—When purified by washing with very dilute sodium hydroxide, wheat, rice, and maize starches are hydrolysable at the same rate by the same kind of amylase, and this is true for a large variety of agents, such as saliva, pancreatin, purified pancreatic amylase, malt extract, purified malt amylase, taka-diaxase, or the purified amylase of *Aspergillus oryzae*. When washed with water only, potato starch

is almost pure, but the cereal starches, especially maize starch, appear to contain fatty or resinous substances which interfere with the hydrolysis, even after the starch has been dissolved in boiling water. These interfering substances are partly removed by ether, but best by dilute alkali hydroxide. Potato starch is slightly more digestible than the purified cereal starches. In one case, however, when purified potato starch was left with purified pancreatic amylase, a much lower rate of hydrolysis was observed, suggesting that some accessory substance had been removed during the purification.

The experiments on which these conclusions are based were carried out as follows. Sufficient of the starch preparations were taken to furnish 1% solutions of real, dry starch, and gelatinised by boiling with water for three minutes. The solutions were then rendered neutral to rosolic acid and made up to 100 c.c. at 40° in a thermostat. Uniform volumes of the enzyme preparations, sufficient to cause hydrolysis to proceed to about one half, were then placed with any necessary salts in several flasks and the starch solutions added. After thirty minutes at 40°, the hydrolysis was stopped by rapidly boiling the mixture, and the reducing sugar was estimated by Fehling's method.

J. C. W.

The Action of Ptyalin. HUGH MCGUIGAN (*J. Biol. Chem.*, 1919, **39**, 273—284).—Chittenden and Smith (*T. Conn. Acad. Arts and Sci.*, 1885, **6**, 343) studied the action of ptyalin on starch and found that a relation between the amount of sugar formed and the amount of ptyalin used existed only when the saliva was diluted 50 to 100 times. These experiments have been in the main confirmed by the author, who has also found that the balance point shifts with the volume of saliva used, and that it may go as high as 75% of the substrate—calculated as dextrose. The products of digestion which interfere with the reaction are not dextrose or maltose. There is evidence that ptyalin combines with starch during digestion, and exerts a force which causes hydrolysis.

J. C. D.

Arsenical Medical Product and Process of Producing Same. J. M. WHITE (U.S. Pat. 1297952).—A product believed to be sodium dimethylphenyl hydrogen arsenide, $C_6H_5Me_2AsHNa$, m. p. about 121°, readily soluble in water, is obtained by the interaction of sodium benzoate and sodium cacodylate in aqueous solution [See, further, *J. Soc. Chem. Ind.*, 1919, 847A.]

Physiological Chemistry.

Concentration of Ammonia in Blood. Comparison with Concentration of Ammonia in Different Secretions and Tissues, especially Muscle Tissue. K. L. GAD-ANDERSEN (*J. Biol. Chem.*, 1919, **39**, 267—271).—A method for the estimation of ammonia in the tissues is described. The author records that he found the concentrations of ammonia in muscle and in blood of the same order. The concentration of ammonia in the heart muscle, liver, fatty tissue, bile, cerebro-spinal fluid, and aqueous humour is the same as in blood. J. C. D.

Some Data concerning the Alleged Relation of Catalase to Animal Oxidations. RAYMOND L. STEHLE (*J. Biol. Chem.*, 1919, **39**, 403—420).—The feeding of meat and the administration of "saccharin," β -hydroxybutyric acid, alanine, and glycine are not accompanied by an increase in the catalase content of the blood to the extent reported by Burge (*Amer. J. Physiol.*, 1918, **46**, 117; 1918—1919, **47**, 13). It is suggested that fluctuations in catalase content are due to fluctuations in the red cell count of the blood, and that catalase content is a function of the number of red cells. J. C. D.

Importance of Accurate and Quantitative Measurements in Experimental Work on Nutrition and Accessory Food Factors. HARRIETTE CHICK and E. MARGARET HUME (*J. Biol. Chem.*, 1919, **39**, 203—207).—The authors point out that much of the experimental work recently published on the subject of the accessory food factors may be criticised on the ground that quantitative measurements have not received sufficient attention. In comparing the value of a series of foodstuffs as regards their value in content of some accessory food factors, it is obvious that the first step necessary is to determine in each case the minimum daily dose which will maintain health in the experimental animal, and to institute comparison between these amounts.

Neglect of this necessary procedure has led to many vague and erroneous results being reported. J. C. D.

Hydrogen- and Hydroxyl-ion Equilibrium in Solutions. I. W. LÖFFLER and K. SPIRO (*Helv. Chim. Acta*, 1919, **2**, 417—419).—Most of the liquids of the animal organism exhibit the same reaction approximating to neutrality, the maintenance of this reaction being of the utmost importance for many physiological processes, and alterations in it being of great influence on the course of essential vital processes. In an investigation of the extent to which the results obtained with colloidal solutions are applicable to solutions of crystalloids, the authors have attained a simple demonstration of the fact that the neutrality of crystalloid solu-

tions is regulated by physico-chemical as well as by chemical factors. In all adsorption processes, specific forces act, different substances showing considerable differences as regards adsorbability. Alteration of the reaction by shaking with animal charcoal is not shown by all solutions used as "moderators" or "buffers"; thus, no such change occurs with phosphate solutions, whereas with solutions of citrates and borates it is easily detectable, the value of p_H being increased with the former and diminished with the latter salts. The use to which animal charcoal is now put in the treatment of infective diseases may depend, not merely on its ability to absorb bacteria and toxins, but also on its action in combating the acidity of the stomach contents arising from bacterial influence.

T. H. P.

Equilibrium between Potassium, Rubidium, Cæsium, and Uranium. (MLLE.) L. KAISER (*Arch. Néerland Physiol.*, 1919, 3, 587—593).—Potassium in Ringer's solution may be replaced by rubidium or cæsium, as far as its action on the isolated frog's heart is concerned. The maximum action is given by the following concentrations, expressed as mg. per litre: potassium 92, rubidium 116, cæsium 78. It has been shown that certain elements, such as uranium, thorium, and radium, which should be capable of replacing potassium, actually exert an opposite effect. This is viewed in the light of the fact that potassium emits negative β -rays, whilst uranium emits positive α -rays. The antagonistic action of these elements on the frog's heart is considered.

J. C. D.

Composition of the Posterior and Anterior Lobes of Cattle Pituitaries. C. G. MCARTHUR (*J. Amer. Chem. Soc.*, 1919 41, 1225—1240).—See this vol., ii, 483.

The Supposed Occurrence of Methylguanidine in Meat, with Observations on the Oxidation of Creatine by Mercuric Acetate. ISIDOR GREENWALD (*J. Amer. Chem. Soc.*, 1919, 41, 1109—1115).—Most of the reports that methylguanidine occurs in meat are based on the use of either silver nitrate and barium hydroxide or mercuric chloride and sodium acetate as the precipitating agents. Ewins has already shown that the former agent is capable of oxidising creatine to methylguanidine (A., 1916, i, 528), and it is now proved that mercuric acetate is equally unsatisfactory, for not only does it fail to give complete precipitation, but it also oxidises creatine to methylguanidine and oxalic acid, and an intermediate product, methylguanidoglyoxylic acid, $NHMe \cdot C(:NH) \cdot NH \cdot CO \cdot CO_2H$. These results have recently been confirmed by Baumann and Ingvaldsen (A., 1918, i, 423).

Using a modification of the process by which Brieger isolated methylguanidine from very putrid meat in connexion with his work on ptomaines, the author has failed to find any of the base in fairly fresh meat.

J. C. W.

Metabolism of Dextrose in Surviving Organs. VII. Action of Muscular Tissue of the Dog (during Feeding and Fasting) on Dextrose Circulating in it and on the Glycogen contained in it. UGO LOMBROSO and LUDOVICO PATERNI (*Arch. farm. sper. sci. aff.*, 1919, **27**, 17—32).—When placed under suitable conditions, the muscular tissue of the dog is able to consume, not merely its own glycogen, but also marked quantities of dextrose added to the liquid circulating through it, such consumption being the greater when the tissue is from a dog being fed than when it is from one kept fasting. T. H. P.

The Salicylates. XI. The Stability and Destruction of the Salicyl Group under Biological Conditions. P. J. HANZLIK and N. C. WETZEL (*J. Pharm. Exp. Ther.*, 1919, **14**, 25—42).—It has been previously reported that 20 to 30% of the salicyl group remains unaccounted for after its passage through the body, and is presumably destroyed (*ibid.*, 1917, **9**, 247). Solutions of sodium salicylate deteriorate when kept, particularly when they are dilute. The decomposition appears to be due to the action of living organisms, and may be inhibited by adding chloroform. Sodium salicylate solutions were found to deteriorate in the presence of yeast, but not as rapidly as when allowed to remain alone. The salicyl group appears to undergo destruction when in the presence of minced tissue. About 20% of salicylates administered to normal individuals is destroyed, whilst in the cat and dog the amount destroyed is much greater.

A general increase in metabolism, such as is encountered in febrile conditions, leads to an increased destruction of the salicyl group. J. C. D.

The Salicylates. XII. The Excretion of Salicyl after Administration of Methyl Salicylate to Animals. P. J. HANZLIK and N. C. WETZEL (*J. Pharm. Exp. Ther.*, 1919, **14**, 43—46).—The excretion of salicyl by animals (dogs and cats) after the administration of methyl salicylate is approximately 25% less than after the administration of sodium salicylate. After gastric administration, the free ester was found in the urine in concentrations of 0.2 to 0.52%, and 14.4% after intramuscular injection. J. C. D.

Chemistry of Vegetable Physiology and Agriculture

Mineral Matter in Plants : The Ashes of some Roots and Tubers. LUCIEN LEROUX and DÉSIÉ LEROUX (*Ann. Chim. anal.*, 1919, [ii], 1, 207—209).—The following amounts of ash were found in the air-dried substances: Potato, 4·05%; common comfrey, 9·06%; dahlia, 5·10%; burdock, 12·25%; thistle, 11·45%; gentian,

3.65%; carrot, 6.25%; turnip, 7.15%; water lily, 3.65%; nettle, 7.83%; male fern, 4.83%. Analyses of the ashes are also given. The largest quantities of sulphuric acid were found in thistle ash and turnip ash (18.5% and 13.2% of SO_3 respectively); phosphoric acid was most abundant in water-lily ash (14.7% P_2O_5), and calcium in gentian ash (19.0% CaO). Gentian ash also yielded the largest quantity of iron, namely, 6.3% Fe_2O_3 . W. P. S.

Carbohydrates of Vegetables. V. Carbohydrates of Carrots. VI. Carbohydrates of Green Peas. ERNST BUSOLT (*J. Landw.*, 1916, **64**, 357—360, 361—362. Compare A., 1914, i, 792).—Carrots (6 kilos. of fresh roots) contain mannitol (23.5 grams) and dextrose (2.8 grams), whilst green peas contain mannitol, dextrose, lævulose, and glycuronic acid. T. H. P.

Secretion of Phosphates in the Stems of Djatikapur [Tectona grandis, L.]. A. WICHMANN (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 968—982).—A discussion on the nature of the mineral deposits found in the stems of teak trees. From a consideration of the data the author concludes that the deposits are hydrated calcium phosphate, and that this may change into calcium magnesium phosphate. The teak tree absorbs more phosphoric acid than any other tree, and the effects of this on the nature of the soil are considered. J. F. S.

Content of Hydrastine and Berberine in Hydrastis canadensis Grown in Austria (at Korneuberg) and Estimation of Berberine. RICHARD WASICKY and MARIANNE JOACHIMOWITZ (*Arch. Pharm.*, 1917, **255**, 497—506).—An accurate method for estimating berberine is described, and also the results of the estimation of hydrastine and berberine in the different parts of *Hydrastis canadensis* grown in Austria. [See *J. Soc. Chem. Ind.*, 1919, 737A.] T. H. P.

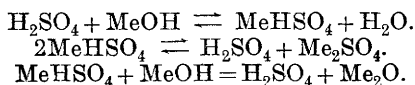
The Action of some Common Soil Amendments. J. E. GREAVES and E. G. CARTER (*Soil Sci.*, 1919, **7**, 121—160).—From a review of the literature on this subject, a full bibliography of which is given, it is shown that the sulphates of magnesium, calcium, and iron, the chlorides of sodium, potassium, magnesium, and calcium, and manganese and iron salts may be especially efficient as soil stimulants. This effect is due in some cases to an increase in the available phosphate, and in others to an increase in the available nitrogen, these increases in available nitrogen and phosphorus being quite sufficient to account for the noted increase in crop yields resulting from the use of these soil amendments. In certain cases, an increase in the organic phosphorus rather than in the available phosphate or nitrogen results from their application. W. G.

Organic Chemistry.

Chlorination of Methane. J. PFEIFER, F. MAUTHNER, and O. REITLINGER (*J. pr. Chem.*, 1919, [ii], **99**, 239—242).—The process has been studied by passing suitable mixtures of chlorine and a natural gas consisting of nearly pure methane, free from ethylene hydrocarbons but containing small amounts of nitrogen and oxygen, over antimony pentachloride or ferric chloride contained in a quartz tube heated at 360—400°. With the former catalyst and the gases mixed in the proportion of one volume of methane to two volumes of chlorine, methylene chloride (5·8%), chloroform (20·3%), carbon tetrachloride (5·9%), and hydrogen chloride (32%) were obtained, 64% of the chlorine entering into action. With ferric chloride and equal volumes of the two gases, the substances formed were methyl chloride (5·8%), methylene chloride (15·7%), chloroform (21·7%), and hydrogen chloride (43·2%), 86·4% of the chlorine being used; when 2 volumes of chlorine were employed for each volume of methane, there were obtained methyl chloride (traces), methylene chloride (13·25%), chloroform (22·2%), carbon tetrachloride (6·35%), and hydrogen chloride (41·8%), 83·6% of the chlorine entering into action. With 2 volumes of methane to 1 volume of chlorine, 30·1% of methyl chloride and a mixture of approximately equal amounts of methylene chloride and chloroform were produced. When the proportion of methane to chlorine was 3:1, the yield of methyl chloride rose to 40% of that theoretically possible. Attempts to secure carbon tetrachloride in good yield by increasing the relative amount of chlorine were rendered difficult by the occurrence of violent explosions; a mixture of chloroform and carbon tetrachloride was, however, obtained by the use of methane (1 vol.) and chlorine (3 vols.) diluted with nitrogen (2 vols.).

H. W.

Action of Concentrated Sulphuric Acid on Methyl Alcohol. J. GUYOT and L. J. SIMON (*Compt. rend.*, 1919, **169**, 655—657).—The yield of methyl sulphate in the action of sulphuric acid on methyl alcohol increases steadily as the molecular proportion of the sulphuric acid in the reacting mixture increases. The complete mechanism of the reaction is given by the three equations:



The combined equilibrium of the first two reactions is, to a large extent, independent of the temperature, but the velocity with which the equilibrium is reached is largely influenced by the temperature.

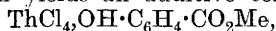
W. G.

Action of Sulphuric Anhydride and of Fuming Sulphuric Acid on Methyl Alcohol. Preparation of Methyl Sulphate.

J. GUYOT and L. J. SIMON (*Compt. rend.*, 1919, **164**, 795—797).—By the action of 60% fuming sulphuric acid on pure methyl alcohol in the calculated proportion, methyl sulphate may readily be obtained, the yield exceeding 90%. An alternative method is to pass the vapour of methyl ether into the acid until the whole of the sulphuric anhydride, which it contains, is converted into methyl sulphate, and then to distil the mixture. [See, further, *J. Soc. Chem. Ind.*, 1919, 924A.] W. G.

Compounds of Thorium. I. Addition and Substitution Compounds of Thorium Chloride.

G. JANTSCH and W. URBACH (*Helv. Chim. Acta*, 1919, **2**, 490—500).—Thorium chloride on boiling with absolute alcohol forms a white, very deliquescent additive compound, $\text{ThCl}_4 \cdot 4\text{EtOH}$; this crystallises in fine, prismatic plates, and slowly loses alcohol on keeping. On shaking anhydrous thorium chloride with acetone, solution occurs after a short time, and on keeping over phosphoric oxide the additive compound, $\text{ThCl}_4 \cdot 2\text{COMe}_2$, separates in small, white, prismatic needles. Heating thorium chloride with acetophenone in chloroform solution gives a clear solution which on keeping over phosphoric oxide yields long, white needles of $\text{ThCl}_4 \cdot 4\text{COPhMe}$, which are very hygroscopic and lose the whole of their acetophenone on keeping. A similar compound, $\text{ThCl}_4 \cdot 4\text{COPh}_2$, is produced when benzophenone is substituted for acetophenone in the last preparation. Thorium acetate is prepared as a white, crystalline mass by heating anhydrous thorium chloride with anhydrous acetic acid. Thorium benzoate is prepared as a white, crystalline precipitate by heating benzoic acid in xylene solution with anhydrous thorium chloride as long as hydrogen chloride is evolved. If, however, the reaction takes place in light petroleum of high boiling point the chlorobenzoate is produced. This compound, $\text{ThCl}(\text{OBz})_3$, is very hygroscopic, and is quite insoluble in benzene and chloroform. When thorium chloride is heated with four molecules of salicylaldehyde in ethereal solution a clear, yellow solution is produced, from which on further heating separates a light yellow, crystalline, additive compound, $\text{ThCl}_4 \cdot 2\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CHO}$. If, however, the ether is replaced by chloroform, the substitution product, $\text{ThCl}_2(\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CHO})_2$, is formed as a canary-yellow, crystalline precipitate, which is very hygroscopic. Thorium chloride heated with three molecules of methyl salicylate in ethereal suspension yields an additive compound,



in fine, white needles; if chloroform, benzene, or xylene is substituted for ether, three substitution products are obtained, depending on the amount of ester employed, (1) with 2 molecules of ester in chloroform the compound $\text{ThCl}_3 \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Me}$ is formed in fine, white needles; (2) with 4 molecules of ester in benzene the compound $\text{ThCl}_2(\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Me})_2$ is formed in white needles; (3) with 6 molecules of ester in xylene a faintly yellow substance,

$\text{ThCl}(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me})_3$, is obtained, which on washing with light petroleum becomes white.

J. F. S.

Ethylene Chlorohydrin and $\beta\beta'$ -Dichloroethyl Sulphide.

M. GOMBERG (*J. Amer. Chem. Soc.*, 1919, **41**, 1414—1431).—An account of work done under the auspices of the American Bureau of Mines, War Gas Investigations. Many of the conclusions are already well known, but they may be summarised as follows.

I. Preparation of Ethylene Chlorohydrin.—In analogy to the reactions between bromine water and ethylene discussed by Read and Williams (T., 1917, **111**, 240), the author expected that the controlling factors would be the velocities of the reactions between ethylene and chlorine or hypochlorous acid, and actually found that by passing the two gases into water, keeping ethylene in slight excess, a concentration of 6—8% of chlorohydrin is reached before an appreciable amount of dichloride is formed. Up to this point the gases are absorbed rapidly at 10—12° (about 20—25 litres of each per hour in the experiments), but thereafter the reaction becomes sluggish. With a slow stream of gas, however, concentrations of chlorohydrin as high as 14—15% may be reached, but always accompanied by much dichloride. The influence of dissolved chlorohydrin, hydrogen chloride, or metallic chlorides on the course of the reaction was roughly determined. Chlorohydrin itself is rather helpful at the outset, and hydrochloric acid up to 2*N*- is no hindrance to the exclusive production of the chlorohydrin. The combined effect, however, is more important, for when both are present in *N*-concentration, the formation of ethylene dichloride is favoured. Metallic salts are much more harmful, and consequently any attempt to neutralise the hydrochloric acid formed during the reaction $[\text{H}_2\text{O} + \text{Cl}_2 \rightleftharpoons \text{HClO} + \text{HCl}]$ does more harm than good. Efficient stirring is obviously most important. Altogether, it is not advisable to aim at more than 8% concentrations of chlorohydrin. The refractive index gives a measure of the concentration (water, 1.333; chlorohydrin, 1.442).

II. Concentration and Isolation of the Chlorohydrin.—A 42.5% solution of chlorohydrin in water has the constant boiling point 95.8°. More dilute solutions can therefore be enriched by distillation, and entirely freed from hydrochloric acid. The effect of salts on the course of the distillation is striking. For example, 9 litres of a 7.3% solution were neutralised with lime and distilled, 4 litres being collected; this was saturated with salt and distilled again, 1.6 litres being collected; this was saturated with calcium chloride and concentrated by distillation to 1 litre, the resulting solution containing nearly all the original chlorohydrin, being 64%. The subject of "salting out" the chlorohydrin appears to offer many interesting problems. Saturation with sodium sulphate at 32—33° seems to offer the best results; the aqueous layer is about 7% chlorohydrin, whilst the separated oil contains about 68% of chlorohydrin and only about 0.65 gram of sodium sulphate per 100 c.c. A combination of distillation, "salting out," and extraction with ether, benzene, or perhaps ethylene dichloride would be the best scheme

for isolating the pure compound. Very little hydrolysis takes place during the distillations.

III. *Conversion into $\beta\beta'$ -Dichloroethyl Sulphide.*—The reaction with sodium sulphide proceeds just as well with 20% solutions of chlorohydrin as with more concentrated solutions, and only a small excess of the salt is required. Concentration being necessary at some point, however, it is best to use 40—80% solutions. After the reaction, which is completed by warming, the solution is neutralised by sulphuric acid and evaporated under reduced pressure, when the thiodiglycol, $S(CH_2 \cdot CH_2 \cdot OH)_2$, may be extracted by alcohol. If the isolation of this is not required, however, 70—80% chlorohydrin is added to solid sodium sulphide, the product is neutralised by 90% sulphuric acid, and then mixed with concentrated hydrochloric acid. The salts are filtered and the solution warmed at 60—75°, when the “mustard gas” separates as an oil almost dry and free from hydrogen chloride, the yield being 90—98%.

In an attempt to prepare $\beta\beta'$ -dichloroethyl sulphide by the interaction of ethylene dichloride and metallic sulphides, it was soon realised that the desired product was more reactive than the parent substance, a disulphide, $(C_2H_4)_2S_2$, being formed when “mustard gas” is even left with sodium sulphide solution in the cold.

J. C. W.

Superpalite [Trichloromethyl Chloroformate]. H. P. HOOD and H. R. MURDOCK (*J. Physical Chem.*, 1919, **23**, 498—512).—The preparation, properties, and decomposition of trichloromethyl chloroformate have been studied. The best method of preparation consists in treating methyl alcohol with carbonyl chloride and chlorinating the product, methyl chloroformate, in bright light with elevation of temperature as the chlorination proceeds. Attempts to prepare this compound directly from carbonyl chloride, or from carbon dioxide and carbon tetrachloride, failed. Trichloromethyl chloroformate is decomposed by charcoal and by ferric oxide into carbonyl chloride. When working in sealed tubes at constant temperature the reaction can be brought to a standstill at any desired point in the presence of iron oxide. Alumina decomposes superpalite into carbon tetrachloride and carbon dioxide. Perchlorodimethyl carbonate breaks up on heating into superpalite and carbonyl chloride. When methyl chloroformate is chlorinated in light at suitable temperatures the products are chloromethyl chloroformate (b. p. 107°), dichloromethyl chloroformate (b. p. 114°), and trichloromethyl chloroformate (b. p. 128°). When methyl carbonate is chlorinated, the successive products are monochloromethyl carbonate, b. p. 138°, dichloromethyl carbonate, b. p. 178°, and hexachloromethyl carbonate, m. p. 78°. J. F. S.

The Catalytic Reduction of Halogenated Acetic Esters.

PAUL SABATIER and A. MAILHE (*Compt. rend.*, 1919, **169**, 758—761).—The halogenated acetic esters may readily be reduced to the corresponding acetic esters by passing their vapours along with hydrogen over reduced nickel at 300°. This method has been

successfully applied to ethyl mono-, di-, and tri-chloroacetates and ethyl bromoacetate, good yields of ethyl acetate being obtained. In the case of the di- and tri-chloroacetates, the removal of the chlorine takes place in successive stages. In each case small amounts of ethylene and acetaldehyde are obtained, due to secondary decomposition of the ethyl acetate.

W. G.

[Preparation of] Acetic Anhydride and Paracetaldehyde from Ethylidene Diacetate. J. KOETSCHET and M. BEUDET (U.S. Pat. 1306963).—A mixture of ethylidene diacetate (400 parts) with sulphuric acid (D 1.87) (8 parts) is heated at 70–80° at a pressure of about 100 mm. In two hours 350 parts of a mixture of paracetaldehyde and acetic anhydride distil, and a residue comprising sulphuric acid and 50 parts of unchanged ethylidene diacetate remains in the reaction vessel. To this 350 parts of ethylidene diacetate may then be added and the reaction continued as before. Distillation is facilitated by passing a current of pure or diluted oxygen into the mixture. The formation of the tarry by-products obtained when higher temperatures are employed in effecting the operation at atmospheric pressure is prevented by conducting the reaction in a vacuum.

CHEMICAL ABSTRACTS.

[Preparation of] Ethylidene Diacetate. J. KOETSCHET and M. BEUDET (U.S. Pat., 1306964).—Mercuric oxide (40 parts) is dissolved in acetic acid (800 parts), the temperature raised to 70°, and a hot solution of β -naphthalenesulphonic acid in acetic acid (200 parts) is added slowly with stirring. A white precipitate of mercuric naphthalenesulphonate is formed. Acetylene is passed into this mixture at 70°, 200 parts being absorbed during two hours. The ethylidene diacetate formed is then separated from the excess of acetic acid. According to a modification of the procedure, mercuric oxide (40 parts) is dissolved in glacial acetic acid (1000 parts) heated at 70°, and into this solution is run a mixture of sulphoacetic acid (26 parts) and acetic acid (100 parts). On passing acetylene into the resulting mixture, 230 parts of acetylene are absorbed in five hours at 65°. The use of mercuric acetate together with aromatic or aliphatic sulphonic acids, instead of mercuric sulphate, as catalyst enables the reaction to be carried out at lower temperatures without deposition of tarry by-products such as are produced when mercuric sulphate is used and the reaction is effected at 90°.

CHEMICAL ABSTRACTS.

The Distillation of Sodium Stearate and Oleate under Reduced Pressure, and the Origin of Petroleum. AMÉ PICTET and JACQUES POTOK (*Helv. Chim. Acta*, 1919, 2, 501–510).—By the distillation of one kilo. of sodium stearate in ten portions, under 12–15 mm., 700 grams of a pasty mass of hydrocarbons are obtained, leaving 200 grams of a residue which contains very little carbon, or salts of the lower fatty acids, being almost entirely sodium carbonate. The distillate consists chiefly of decane, b. p. 172–175°, tetradecane, b. p. 235–238°, pentadecane, b. p.

257—260°, with tetratriacontane, b. p. above 360°, m. p. 73·5°, as the main constituent, and obviously the primary product. No unsaturated or cyclic hydrocarbons are present. The physical properties of the four hydrocarbons agree with the data assigned by Mabery to specimens isolated from Pennsylvanian petroleum. Dry sodium oleate also gives a 70% yield of oil under these conditions, but all the fractions are ethylenic. The chief hydrocarbons found are nonylene, b. p. 145—148°, decylene, b. p. 160—163°, D_4^{20} 0·7630, n_D^{20} 1·4301, undecylene, b. p. 195—198°, and tridecylene, b. p. 228—231°, agreeing in physical properties with the olefines isolated by Coates and Mabery from American petroleum. No naphthenes are present.

The results therefore confirm Engler's hypothesis, in so far as the open-chain hydrocarbons are concerned, namely, that they originate from the fats of marine plants and animals. As the conditions of the decompositions now effected are about as mild as they could very well be, the absence of any traces of cyclic hydrocarbons, especially optically active naphthenes, would strongly suggest a totally different origin for such substances in natural petroleum, and the authors regard the resins and terpenes as the source.

J. C. W.

The Direct Replacement of Glycerol in Fats by Higher Polyhydric Alcohols. I. Interaction of Olein and Stearin with Mannitol. ARTHUR LAPWORTH and LEONORE KLETZ PEARSON (*Biochem. J.*, 1919, **13**, 296—300).—Glycerol can be quantitatively replaced by mannitol in fats by heating the fat with mannitol in the presence of sodium ethoxide under reduced pressure. An almost theoretical yield of glycerol is obtained in the distillate, whilst the residue in the distillation flask may be treated so as to obtain a synthetic mannitol fat. The maximum yield of glycerol is obtained when the proportion is two molecules of fat to three of mannitol. The mannitol compounds formed appear to be mixtures of di-oleates (or di-stearates) of mannitan or isomannide.

J. C. D.

The Walden Inversion. P. KARRER and W. KAASE (*Helv. Chim. Acta*, 1919, **2**, 436—454).—Various reactions in the glutaric acid series have been studied, with particular reference to the measurement of the rotations of the products for light of different wave-lengths, from about 656 $\mu\mu$ to 461 $\mu\mu$. When the rotations for sodium light only are examined, a fairly regular, but meaningless, fluctuation from *d*- to *l*- is observed, but when the rotation-dispersion curves are considered, a completely different conception of the changes may be formed. Thus, of all the following compounds, formed in the order named, and given the sign of rotation for sodium light, namely, *d*-glutamic acid, *l*- α -chloroglutaric acid, zinc *d*- α -hydroxyglutarate, *l*- α -hydroxyglutaric acid, *d*-butyrolactone- γ -carboxylic acid, and also the ethyl *l*-pyroglutamate formed from the initial acid and the *d*-silver salt of the butyrolactone- γ -carboxylic acid obtained from the *l*-chloroglutaric acid, the only product which gives higher negative rotations the shorter the wave-length,

is the α -chloroglutaric acid. All the others give rotation-dispersion curves which tend to rise to highest points in the positive field. It appears, therefore, that only in the replacements of the amino-group by halogen, and this by hydroxyl, are there any changes in configuration, which is, of course, plausible, for these are the only changes directly affecting the asymmetric carbon atom. The authors go so far as to suggest that the symbol d - should be given to those compounds which tend to give positive maxima for their rotations, and l - to those which give negative maxima.

To a certain extent, the results and views expressed agree with those of Clough (T., 1918, **113**, 526). In one particular, however, there is contradiction. Clough states that phosphorus pentachloride and thionyl chloride produce from α -hydroxy-aliphatic acids chloro-acids of the same configuration, whereas nitrosyl chloride acting on α -amino-acids gives chloro-acids of opposite sign, and the exchange of halogen by hydroxyl, with silver oxide, is accompanied by another change of sign. If both statements are true, a l -chloro-acid should give a d -hydroxy-acid, and this a d -chloro-acid, but in the present case it is found that l - α -chloroglutaric acid may be converted into the d -hydroxy-acid and this reconverted into the l - α -chloro-acid by phosphorus pentachloride.

Similar regularities in their rotation-dispersion curves are shown by aspartic acid and its derivatives. The rotations of the so-called l -aspartic acid, its ester and the so-called l -malic acid obtained indirectly from it tend to a positive maximum, whereas the l -chlorosuccinic acid intermediate between the aspartic and malic acids tends to a negative maximum. Therefore, l -aspartic and l -malic acids should be called d -acids. The rotation of malic acid is difficult to judge, for it depends so much on concentration. The authors have chosen 25% solutions as the maximum concentration for which the curve is normal, but it is obvious that if the direction of the rotation-dispersion curve is to be a test of the configuration, the conditions of solvent, concentration, and temperature must be so chosen that the curve is as characteristic as possible for the compound under examination.

The following table gives the specific rotations at 14° for the

Substance.	C.	D.	Hg.	F.
New designation	656.3	589.3	546.3	486.1 μ
d -Glutamic acid	+8.05°	+10.52°	+12.96°	+17.53°
Ethyl d -pyroglutamate	-3.40	-2.68	-1.59	+1.99
l - α -Chloroglutaric acid	-18.26	-22.67	-26.81	-34.67
d - α -Hydroxyglutaric acid	-2.00	-1.34	-0.67	+0.67
Silver d -butyrolactone- γ -carb-oxylate	+5.67	+8.59	+9.14	+13.16
* d -Butyrolactone- γ -carboxylic acid	+1.11	+2.14	+2.83	+3.66
†	-0.33	+2.67	+3.33	+4.17
‡Zinc d - α -hydroxyglutarate.....	+4.24	+6.65	+8.24	—
§ d -Aspartic acid.....	-3.54	-2.48	-2.13	—
Ethyl d -aspartate	+0.98	+1.73	+2.25	+3.38
l -Chlorosuccinic acid	-15.04	-18.92	-22.96	-30.90

* From zinc α -hydroxyglutarate.

‡ At 16° .

† From the silver salt.

§ In dil. NaOH (3 mol.).

principal lines; for others, and for the curves, the original should be consulted.

J. C. W.

Bile Acids. V. The Reduction of Dehydrocholic and Dehydrodeoxycholic Acids. HEINRICH WIELAND and ERICH BOERSCH (*Zeitsch. physiol. Chem.*, 1919, **106**, 190—201).—*Dehydroisodeoxycholic acid* (β -diketocholanic acid), $C_{24}H_{36}O_4$, was prepared as its ethyl ester by reducing an alcoholic solution of dehydrocholic acid with granulated zinc and hydrochloric acid in presence of mercuric chloride; it crystallises in colourless needles, m. p. 177° ; the *ethyl* ester forms lustrous needles, m. p. 152.5° .

Cholanic acid, $C_{24}H_{40}O_2$, is obtained from dehydrocholic acid by boiling with zinc amalgam and concentrated hydrochloric acid for twelve hours, and then passing hydrogen chloride into the boiling solution for ten hours. The *ethyl* ester crystallises in shining fragments, m. p. $93-94^\circ$, $[\alpha]_D^{19} + 20.97^\circ$. The acid forms voluminous clusters of needles, m. p. $163-164^\circ$, $[\alpha]_D^{14} + 21.74^\circ$ in chloroform solution.

α -Ketocholanic acid, $C_{24}H_{38}O_3$, is obtained as the ethyl ester, by reducing an alcoholic solution of dehydrodeoxycholic acid with zinc amalgam and concentrated hydrochloric acid. The *ethyl* ester forms colourless needles, m. p. 95° ; the acid crystallises in broad, colourless leaves, m. p. 183° .

Hydroxyketocholanic acid, $C_{24}H_{38}O_4$, also obtainable by reduction of dehydrodeoxycholic acid, forms soft, lustrous needles, m. p. 161° ; the *ethyl* ester forms lustrous prisms, m. p. 133° .

S. S. Z.

The Oxidation of Organic Compounds with Alkaline Potassium Permanganate. I. The Oxidation of Acetaldehyde. II. The Oxidation of Ethylene Glycol, Glycollaldehyde, Glyoxal, Glycollic Acid, and Glyoxylic Acid.

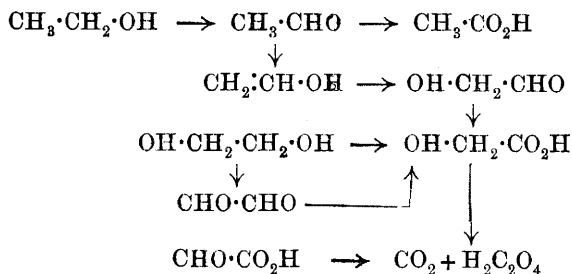
WILLIAM LLOYD EVANS and HOMER ADKINS (*J. Amer. Chem. Soc.*, 1919, **41**, 1385—1414. Compare this vol., i, 514).—I. A solution of potassium permanganate, containing 15 grams per litre and various proportions of potassium hydroxide, was reduced by a 2-molar solution of acetaldehyde at 25° , 50° , and 75° , the quantity of aldehyde being recorded, and also the weights of the various oxidation products. The results are tabulated and reproduced by curves. Within certain limits, the quantity of acetic acid produced is a function of the concentration of potassium hydroxide. When plotted on logarithmic paper, the concentrations fall on a straight line, from which the equation $\log Y = \log B - a \log X$ may be deduced, where Y = the number of grams of acetic acid produced by the oxidation of 0.1 gram.-mol. of acetaldehyde at a concentration of X grams of potassium hydroxide per litre and a = the tangent of the angle which the line makes with the X axis. The limits are as follows: at 25° , 1.95 to 90 grams; at 50° , 1.3 to 32.5 grams; at 75° , 0.85 to 18.5 grams. Below the smaller values, the

oxidation to acetic acid is quantitative; above the higher values, the concentration of alkali has no influence on the yield of acetic acid. Within these limits, the yield of acetic acid decreases with increasing alkalinity and rise of temperature. The other oxidation products are oxalic acid and carbon dioxide. These increase with rise of temperature and alkalinity, but again there are limits above which the concentration of alkali is immaterial. The most instructive reproduction of the yields of these products is given in curves connecting the alkali concentrations with the weights of oxalic acid or carbon dioxide which would be produced if 0.1 molar quantities of acetaldehyde or an intermediate compound were oxidised to oxalic acid and carbon dioxide in the ratio in which they are produced in the particular experiment. For example, if in a given experiment 1 gram of oxalic acid and 1 gram of carbon dioxide were produced, the acetaldehyde equivalent would be 0.49 and 0.50 gram respectively. Then, if a total of 0.99 gram of acetaldehyde produces 1 gram of oxalic acid, 4.4 grams (0.1 mol.) would yield 4.44 grams. The ratio of oxalic acid to carbon dioxide rises with increase of temperature and alkalinity, but the curves connecting alkali concentrations with the above quantities are straight lines if plotted on logarithmic paper. That is, the weight of substance converted into oxalic acid or carbon dioxide compared with the total amount converted into oxalic acid plus carbon dioxide is a simple function of the alkali concentration. In other words, the alkali acts in the same general way on the precursor of these products as it does on the acetaldehyde from which the acetic acid is formed.

II. The oxidation of ethylene glycol, glycollaldehyde, glyoxal, glycollic acid, and glyoxylic acid was studied at 50° in the same manner. Ethylene glycol yields carbon dioxide and oxalic acid; with less than 0.5 gram of potassium hydroxide per litre, the sole product appears to be carbon dioxide, then up to 3 grams per litre the yield of carbon dioxide falls and that of oxalic acid rises uniformly, after which the concentration of alkali has no influence on the ratio between the two products. Glycollaldehyde also produces carbon dioxide in falling amounts and oxalic acid in increasing quantities, but the yields are logarithmic functions of the alkali concentration. Glyoxal behaves more like ethylene glycol; the yields are linear functions of the alkali concentrations up to 45.5 grams potassium hydroxide per litre, when further alkali is without effect on the yields, that of oxalic acid being 76.7%. Glycollic acid yields the same proportions of oxalic acid and carbon dioxide regardless of whether the initial concentration of potassium hydroxide is 0.68 or 48 grams per litre. Glyoxylic acid corresponds with glycollaldehyde; the yields are logarithmic functions of the alkali concentrations.

The curves connecting the yields of oxalic acid and carbon dioxide at 50° with alkali concentrations are absolutely identical in the cases of acetaldehyde and glycollaldehyde. It is therefore highly probable that glycollaldehyde is an intermediate product in the oxidation of acetaldehyde by alkaline permanganate, and the

whole scheme for the oxidation of these compounds with two carbon atoms may be written thus:



J. C. W.

The Stabilisation of Acraldehyde. I. The Methods of Spontaneous Alteration of Acraldehyde. CHARLES MOUREU and CHARLES DUFRAISSE (*Compt. rend.*, 1919, **169**, 621—626).—Acraldehyde, when kept, undergoes spontaneous change in one of two directions, giving either an insoluble resin, disacryl, or a soluble resin. The velocity of change into the insoluble resin is accelerated by the presence of impurities, by rise in temperature, or by an increase in the intensity of illumination. The cause of the fracture of glass vessels in which this change occurs is shown to be purely physical.

The second change into a soluble resin is accelerated by the presence of a free base, metallic salts, or certain compounds, such as hydrogen sulphide, the chlorides of arsenic, antimony, bismuth, or tin, and nitrogenous organic substances. Rise in temperature also accelerates the change.

These two different methods of spontaneous alteration of acraldehyde cannot, apparently, proceed simultaneously in the same sample, although in some cases one change may proceed for a time and then be replaced by the other.

W. G.

The Stabilisation of Acraldehyde. II. Empirical Process of Stabilisation. CHARLES MOUREU and ADOLPHE LÉPAPE (*Compt. rend.*, 1919, **169**, 705—708. Compare Moureu and Dufraisse, preceding abstract).—The process of stabilisation recommended is to shake the crude acraldehyde, prepared by the dehydration of glycerol, with 10% of its weight of dry sodium hydrogen carbonate. The product thus obtained is stable for a long time if it is kept in the absence of air, not exposed to sunlight, and at a temperature not exceeding 30°. The crude acraldehyde contains certain impurities which tend to prevent its conversion into insoluble resin, whilst other impurities accelerate its conversion into soluble resin.

W. G.

Preparation of Anhydrous Dextrose Sodium Iodide. JOHANN A. WÜLFING (D.R.-P. 312643; from *Chem. Zentr.*, 1919, iv, 147).—Anhydrous dextrose and anhydrous sodium iodide, in

the proportion of at least two molecules of the former to one molecule of the latter, are mixed as intimately as possible, and the mixture is melted or moistened with strong alcohol and dried at 100—115°. In either case, the proportion of two molecules of dextrose may be exceeded, whereby the mass becomes more easily melted or pulverised. The double compound, $(C_6H_{12}O_6)_2 \cdot NaI$, exists in the anhydrous and hydrated states ($+ H_2O$). In the former condition it is not hygroscopic, whilst in the latter state it is as hygroscopic as sodium iodide. The yield of the anhydrous substance is quantitative, whilst that obtained in accordance with D.R.-P. 196605 (A., 1908, i, 765) is considerably smaller.

H. W.

Solubility of Lactose. Action of Acids and Alkalis on Lactose. E. SAILLARD (*Chim. et Ind.*, 1919, 2, 1035—1036).—The solubility of lactose at various temperatures was found to be as follows, the solubility of sucrose under the same conditions below given for comparison:

Temperature.	Kilo. of sugar per 1 kilo. of water.	
	Anhydrous Lactose.	Sucrose.
21.5°	0.20	2.06
28.0	0.24	2.16
38.0	0.307	2.34
48.0	0.421	2.55
57.0	0.56	2.78
65.0	0.77	3.03

Lactose is hydrolysed completely in ninety minutes when heated at 90° with 10% hydrochloric acid, but is not appreciably attacked by 10% acetic acid. When lactose is heated at 90° with 1% sodium hydroxide solution, about 64% of the alkali is neutralised and 85% of the sugar destroyed within two hours.

W. P. S.

Predominating Influence of the Degree of Dispersion of Starch Solutions on the so-called Starch Coagulation.

HERMANN SALLINGER (*Kolloid Zeitsch.*, 1919, 25, 79—81).—The coagulation of solutions of soluble starch by means of ptyalin (from human saliva) has been investigated. It is shown that the coagulation takes place sooner the larger the quantity of ptyalin added, and that the amount of coagulated starch decreases, whilst the quantity of maltose formed increases with the amount of ptyalin added. A similar starch solution heated to 110° under a pressure of 1.5 atms. before treatment was coagulated much more slowly, gave about a quarter as much coagulum, but rather more maltose, than the unheated starch. The experiments show the influence of the dispersity on the coagulation, and they also confirm the view of Lintner that it is unnecessary to assume the presence of an enzyme amylocoagulase in malt extract which is capable of affecting the coagulation of starch. The coagulation is brought about by the conversion of the protecting colloid, the starch sol, into sugar, which thereby causes the starch gel to coagulate.

J. F. S.

Synthesis of Polypeptides of which Cystine forms a Constituent. E. ABDERHALDEN and HANS SPINNER (*Zeitsch. physiol. Chem.*, 1919, **106**, 296—309).—The following polypeptides have been synthesised:

Dichloroacetyl-l-cystine crystallises from ethyl acetate in clusters of fan-shaped prisms, m. p. 137—139°, or from water in silky spheres of long needles with one molecule of water, m. p. 96—98°. It shows weak mutarotation.

Diglycyl-l-cystine, a white, amorphous powder, decomposes at 200°, and has $[\alpha]_D^{17} - 111.4^\circ$ to -116.54° in aqueous solution.

Di- α -bromo-d-isohexoyldiglycyl-l-cystine is a yellowish-white powder, and in alcoholic solution has $[\alpha]_D^{19} - 8.37^\circ$ to -18.2° .

Di-l-leucyldiglycyl-l-cystine turns brown at 220°, and in aqueous solution has $[\alpha]_D^{18} - 78.6^\circ$ to -80.99° .

Dichloroacetyldi-l-leucyldiglycyl-l-cystine is a light yellow powder, and in alcoholic solution has $[\alpha]_D - 32.8^\circ$ to -42.85° .

Diglycyldi-l-leucyldiglycyl-l-cystine, a light yellow powder, has in aqueous solution $[\alpha]_D^{20} - 81.78^\circ$.

Dibromo-d-isohexoyldiglycyldi-l-leucyldiglycyl-l-cystine forms a yellow powder.

The action of alcoholic-aqueous ammonia and of alcoholic ammonia on dichloroacetyl-l-cystine is described. S. S. Z.

Bile Acids. IV. The Synthesis of Glycodeoxycholic and Taurodeoxycholic Acids. HEINRICH WIELAND [with FR. L. HEDWIG STENDER] (*Zeitsch. physiol. Chem.*, 1919, **106**, 181—190. Compare A., 1916, i, 710).—*Deoxycholic acid hydrazide*, $C_{24}H_{42}O_3N_2$, prepared from the acid deoxycholic ester and hydrazine hydrate, forms colourless needles, m. p. 208°. The hydrazide was then converted into the amorphous *azide* by treating it with hydrochloric acid and sodium nitrite. From the azide, *glycodeoxycholic acid* was synthesised by a modification of the method which Bondi and Müller used in the preparation of glycocholic acid; it forms colourless needles, m. p. 187—188° (decomp.), and contains one molecule of water, which is lost on heating at 150° in a vacuum.

Taurodeoxycholic acid, $C_{33}H_{50}O_2 \cdot CO \cdot NH \cdot CH_2 \cdot CH_2 \cdot SO_3H$, was prepared from deoxycholic acid azide in the form of colourless, hygroscopic, prismatic needles grouped in rosettes, m. p. 175—200°, not sharp.

Attempts to prepare glycocholeic and taurocholeic acids by combining the conjugated deoxycholic acids with stearic acid failed. The nature and origin of the glycocholeic and taurocholeic acids prepared from the bile are discussed. S. S. Z.

Crystallography of some Platinithiocyanates of Organic Bases. E. QUERCIGH (*Riv. Min. Crist. Ital.*, 1915, **44**, 17—25).—The guanidine salt is trigonal, the piperidine salt hexagonal-pyramidal, and the diacetoneamine salt monoclinic. Complete crystallographic data are given. CHEMICAL ABSTRACTS.

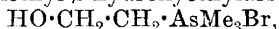
Oxidation Potential of Ferri-Ferrocyanide Solution. I. M. KOLTHOFF (*Chem. Weekblad*, 1919, **16**, 1406—1415).—The influence of the hydrogen ions on the oxidation potential of solutions of potassium ferri-ferrrocyanide has been investigated by the author. A considerable increase of potential was obtained by the addition of even 0.012*N*-hydrogen chloride, and, taking the average for various determinations with different concentrations of hydrochloric acid, it was found that $\epsilon = 0.416 - 0.0577 \log (\text{HCl})^{2.22}$. The influence of the acid is explained by the fact that the third and fourth dissociation constants of hydroferrocyanic acid are comparatively small, whilst hydroferricyanic acid is a strong acid. The concentration of the ferrocyanide ions thus becomes much lower on acidifying. The fourth dissociation constant of hydroferrocyanic acid is about 5×10^{-4} .

The author found no difference in the physical properties (except the colour) of solutions of α - and β -potassium ferrocyanide.

References to the results of other investigators are given.

W. J. W.

Ethanoltrialkylarsonium Hydroxides. M. GUGGENHEIM and E. HUG (U.S. Pat. 1308413).—Trimethyl- β -bromoethylarsonium bromide, prisms, m. p. 239°, is prepared by heating 5 parts of trimethylarsine and 7.5 parts of ethylene dibromide for three hours at about 100°. Three parts of this product may be hydrolysed by heating with 10 parts of water at 180° for four hours. Ethanoltrimethylarsonium [trimethyl- β -hydroxyethylarsonium] bromide,



thus formed, is converted into the free base by the action of silver oxide. β -Bromotetraethylarsonium bromide, prismatic crystals, m. p. 225°, may be obtained similarly from triethylarsine. The product may be hydrolysed to form β -hydroxytetraethylarsonium bromide, and the latter can be converted into the free base by the action of silver oxide. Trimethyl- β -hydroxyethylarsonium hydroxide is a syrup which partly crystallises and has an odour like that of trimethylarsine. It is readily soluble in water or alcohol, and forms a crystalline chloride, m. p. 220°, which is soluble in alcohol.

CHEMICAL ABSTRACTS.

Ethanoltrialkylarsonium Compounds. M. GUGGENHEIM and E. HUG (U.S. Pat. 1308414).—Eighteen parts of trimethylarsine and 20 parts of ethylene chlorohydrin are heated together at 120—125° for four hours. The product, which is partly solidified, is dissolved in alcohol, and, after concentration of the solution, ether is added to precipitate ethanoltrimethylarsonium [trimethyl- β -hydroxyethylarsonium] chloride, $\text{OH}\cdot\text{C}_2\text{H}_4\cdot\text{AsMe}_3\text{Cl}$, which may be converted into the hydroxide by the action of silver oxide. Ethylene bromohydrin may be used instead of the chlorohydrin in effecting the reaction. Triethylarsine, when used as starting material, yields similar products, containing ethyl instead of

methyl. The ethanoltrialkylarsonium hydroxides and their salts are stated to possess valuable therapeutic properties.

CHEMICAL ABSTRACTS.

Relations between the Constitution and the Physical Properties of the Hydrocarbons of the Benzene Series.

K. VON AUWERS (*Annalen*, 1919, **419**, 92—120. Compare A., 1916, i, 130).—Examination of the physical constants of twenty-four hydrocarbons has shown that the compounds with ortho-side-chains occupy a peculiar position; whilst the density and refractive index are higher than those of their isomerides, the exaltations of refractive and dispersive power are lower. In general, the boiling points of ortho-derivatives are higher than those of the isomeric hydrocarbons, although the differences are frequently small. The differences between the constants of ortho- and vicinal derivatives and those of their isomerides are much greater than the small discrepancies observed between different specimens of the same substance as far as carefully purified material and accurate observation are concerned. The influences of constitution on the refractive and dispersive powers of position isomeric aromatic hydrocarbons can only be detected with certainty in the cases of substances with neighbouring side-chains; the differences caused in the meta- and para-series lie within the limits of experimental error.

The methods chiefly used in the preparation of the hydrocarbons are the Fittig synthesis, the elimination of amino-groups from the corresponding amines by Friedländer's method, and the reduction of suitable ketones with amalgamated zinc and hydrochloric acid according to Clemmensen. The following constants are recorded.

Benzene has b. p. 80° , D_4^{13} 0.8867, D_4^{20} 0.880, n_D^{23} 1.50119, $n_D^{12.3}$ 1.50565, $n_D^{16.35}$ 1.51817, $n_D^{12.3}$ 1.52867, n_D^{20} 1.5022. Toluene has b. p. $109-110^{\circ}$, D_4^{13} 0.8684, D_4^{20} 0.866, $n_D^{16.35}$ 1.49365, $n_D^{16.35}$ 1.49782, $n_D^{16.35}$ 1.50967, $n_D^{16.35}$ 1.51970, n_D^{20} 1.4962. Ethylbenzene has b. p. $135-136^{\circ}$, $D_4^{14.5}$ 0.8708, D_4^{20} 0.866, $n_D^{14.5}$ 1.49423, $n_D^{14.5}$ 1.49828, $n_D^{14.5}$ 1.50953, $n_D^{14.5}$ 1.51904, n_D^{20} 1.4960. Propylbenzene has b. p. $158-159^{\circ}$, $D_4^{12.25}$ 0.8681, D_4^{20} 0.862, $n_D^{12.25}$ 1.49176, $n_D^{22.15}$ 1.49549, $n_D^{12.25}$ 1.50630, $n_D^{12.25}$ 1.51533, n_D^{20} 1.4920. *iso*Propylbenzene has b. p. $152.8-153.4^{\circ}$, $D_4^{16.8}$ 0.8662, D_4^{20} 0.864, $n_D^{16.8}$ 1.49063, $n_D^{16.8}$ 1.49441, $n_D^{16.8}$ 1.50539, $n_D^{16.8}$ 1.51466, n_D^{20} 1.4930.

For *o*-xylene the following data are given: I. Commercial specimen rectified over sodium, b. p. $142-142.5^{\circ}$, $D_4^{17.9}$ 0.8798, D_4^{20} 0.878, $n_D^{17.9}$ 1.50090, $n_D^{17.9}$ 1.50491, $n_D^{17.9}$ 1.51668, $n_D^{17.9}$ 1.52659, n_D^{20} 1.5040. II. Specimen from *o*-iodotoluene, methyl iodide, and sodium in warm ethereal solution: b. p. 142° , $D_4^{16.1}$ 0.8825, D_4^{20} 0.879, $n_D^{16.1}$ 1.50248, $n_D^{16.1}$ 1.50664, $n_D^{16.1}$ 1.51846, $n_D^{16.1}$ 1.52838, n_D^{20} 1.5049. III. Specimen from pure *o*-3-xylidine through the diazo-compound: b. p. $142-143^{\circ}$, $D_4^{15.5}$ 0.8837, D_4^{20} 0.880, $n_D^{15.5}$ 1.50368, $n_D^{15.5}$ 1.50777, $n_D^{15.5}$ 1.51960, $n_D^{15.5}$ 1.52958, n_D^{20} 1.5057. *m*-Xylene, prepared from *m*-xylylic acid, has b. p. $135-136^{\circ}$, $D_4^{17.2}$ 0.8666, $D_4^{17.1}$ 0.8667, D_4^{20} 0.864, $n_D^{17.1}$ 1.49429, $n_D^{17.1}$ 1.49830, $n_D^{17.1}$ 1.51007, $n_D^{17.1}$ 1.51997, n_D^{20} 1.4970, whilst when prepared from *m*-xylidine it has b. p. 137.5° , $D_4^{14.85}$ 0.8686,

D_4^{20} 0.865, $n_a^{14.85}$ 1.49548, $n_D^{14.55}$ 1.49962, $n_\beta^{14.85}$ 1.51128, $n_\gamma^{14.85}$ 1.52112, n_D^{20} 1.4973. For *p*-xylene the following constants are recorded: I. Museum specimen, b. p. 135—136°, $D_4^{17.2}$ 0.8627, $D_4^{17.5}$ 0.8625, D_4^{20} 0.861, $n_a^{17.5}$ 1.49273, $n_D^{17.5}$ 1.49682, $n_\beta^{17.5}$ 1.50849, $n_\gamma^{17.5}$ 1.51841, n_D^{20} 1.4957. II. Kahlbaum's product distilled over sodium, b. p. 136—137°, $D_4^{16.1}$ 0.8659, $D_4^{16.2}$ 0.8658, D_4^{20} 0.863, $n_a^{16.2}$ 1.49357, $n_D^{16.2}$ 1.49760, $n_\beta^{16.2}$ 1.50925, $n_\gamma^{16.2}$ 1.51907, n_D^{20} 1.4959. III. Specimen from *p*-dibromobenzene, b. p. 135—136°, $D_4^{16.2}$ 0.8624, D_4^{20} 0.859, $n_a^{16.2}$ 1.49335, $n_D^{16.2}$ 1.49734, $n_\beta^{16.2}$ 1.50912, $n_\gamma^{16.2}$ 1.51902, n_D^{20} 1.4956.

o-Methylethylbenzene has b. p. 164.8—165°, $D_4^{15.7}$ 0.8841, D_4^{20} 0.881, $n_a^{15.7}$ 1.50213, $n_D^{15.7}$ 1.50611, $n_\beta^{15.7}$ 1.51745, $n_\gamma^{15.7}$ 1.52693, n_D^{20} 1.5042. *m*-Methylethylbenzene has b. p. 161.5—162.5°, $D_4^{17.9}$ 0.8690, D_4^{20} 0.867, $n_a^{17.9}$ 1.49456, $n_D^{17.9}$ 1.49849, $n_\beta^{17.9}$ 1.50973, $n_\gamma^{17.9}$ 1.51920, n_D^{20} 1.4975. *p*-Methylethylbenzene (from *p*-bromotoluene) has b. p. 161—162°, $D_4^{22.3}$ 0.8601, $D_4^{22.8}$ 0.8597, D_4^{20} 0.862, $n_a^{22.8}$ 1.48921, $n_D^{22.8}$ 1.49303, $n_\beta^{22.8}$ 1.50417, $n_\gamma^{22.8}$ 1.51353, n_D^{20} 1.4943, whilst when prepared from *p*-tolyl methyl ketone it has b. p. 161—162°, $D_4^{13.1}$ 0.8687, ($D_4^{13.4}$ 0.8685), D_4^{20} 0.863, $n_a^{13.4}$ 1.49588, $n_D^{13.4}$ 1.50004, $n_\beta^{13.4}$ 1.51136, $n_\gamma^{13.4}$ 1.52116, n_D^{20} 1.4971.

o-Methylpropylbenzene has b. p. 184°, $D_4^{15.75}$ 0.8770, D_4^{20} 0.874, $n_a^{15.75}$ 1.49765, $n_D^{15.75}$ 1.50139, $n_\beta^{15.75}$ 1.51218, $n_\gamma^{15.75}$ 1.52125, n_D^{20} 1.4995. *m*-Methylpropylbenzene has b. p. 181.5—182.5°, D_4^{17} 0.8648, D_4^{20} 0.862, n_a^{17} 1.49262, n_D^{17} 1.49640, n_β^{17} 1.50738, n_γ^{17} 1.51646, n_D^{20} 1.4951. *p*-Methylpropylbenzene has b. p. 182—183°, $D_4^{15.4}$ 0.8642, D_4^{20} 0.861, $n_a^{15.4}$ 1.49371, $n_D^{15.4}$ 1.49749, $n_\beta^{15.4}$ 1.50863, $n_\gamma^{15.4}$ 1.51804, n_D^{20} 1.4954.

o-Methylisopropylbenzene (*o*-cymene) has b. p. 175—176°, $D_4^{16.15}$ 0.8789, D_4^{20} 0.876, $n_a^{16.15}$ 1.49826, $n_D^{16.15}$ 1.50206, $n_\beta^{16.15}$ 1.51290, $n_\gamma^{16.15}$ 1.52185, n_D^{20} 1.5003. *m*-Methylisopropylbenzene has b. p. 175°, $D_4^{17.05}$ 0.8628, D_4^{20} 0.860, $n_a^{17.05}$ 1.49016, $n_D^{17.05}$ 1.49385, $n_\beta^{17.05}$ 1.50452, $n_\gamma^{17.05}$ 1.51336, n_D^{20} 1.4925. *p*-Methylisopropylbenzene, from toluene, isopropyl bromide, and aluminium chloride, has b. p. 175—176°, $D_4^{15.0}$ 0.8631, D_4^{20} 0.859, n_a^{15} 1.49105, n_D^{15} 1.49474, n_β^{15} 1.50537, n_γ^{15} 1.51449, n_D^{20} 1.4925; the physical constants are also recorded for specimens obtained commercially, from camphor and phosphoric oxide, from α -terpineol by Wallach's method, and from 1-methyl-4- $\beta\beta$ -dichloroisopropylbenzene by reduction with sodium and alcohol.

p-Diethylbenzene has b. p. 183°, $D_4^{16.3}$ 0.8678 ($D_4^{16.2}$ 0.8679), D_4^{20} 0.865, $n_a^{16.2}$ 1.49499, $n_D^{16.2}$ 1.49897, $n_\beta^{16.2}$ 1.50993, $n_\gamma^{16.2}$ 1.51924, n_D^{20} 1.4973. Hemimellitene has b. p. 175—176°/744 mm., $D_4^{19.55}$ 0.8949, D_4^{20} 0.895, $n_a^{19.55}$ 1.50930, $n_D^{19.55}$ 1.51335, $n_\beta^{19.55}$ 1.52503, $n_\gamma^{19.55}$ 1.53483, n_D^{20} 1.5132. ψ -Cumene has b. p. 168.7—169.2°, $D_4^{15.3}$ 0.8794, D_4^{20} 0.876, $n_a^{15.3}$ 1.50259, $n_D^{15.3}$ 1.50672, $n_\beta^{15.3}$ 1.51841, $n_\gamma^{15.3}$ 1.52816, n_D^{20} 1.5046. Mesitylene has b. p. 165—166°, $D_4^{17.05}$ 0.8646, D_4^{20} 0.862, $n_a^{17.05}$ 1.49403, $n_D^{17.05}$ 1.49804, $n_\beta^{17.05}$ 1.50936, $n_\gamma^{17.05}$ 1.51891, n_D^{20} 1.4967.

1 : 2 : 3 : 4-Tetramethylbenzene has b. p. 203—204°, D_4^{16} 0.9044, D_4^{20} 0.901, n_a^{16} 1.51621, n_D^{16} 1.52031, n_β^{16} 1.53192, n_γ^{16} 1.54189, n_D^{20} 1.5185. 1 : 2 : 5-Trimethyl-4-ethylbenzene has b. p. 211°, $D_4^{15.85}$ 0.8866, ($D_4^{15.75}$ 0.8867), D_4^{20} 0.883, $n_a^{15.75}$ 1.50654, $n_D^{15.75}$ 1.51047, $n_\beta^{15.75}$ 1.52163, $n_\gamma^{15.75}$ 1.53112, n_D^{20} 1.5086. 1 : 3 : 5-Trimethyl-2-ethylbenzene has b. p. 210.2°/753 mm., $D_4^{16.35}$ 0.8885, D_4^{20} 0.886, $n_a^{16.35}$ 1.50875, $n_D^{16.35}$ 1.51274, $n_\beta^{16.35}$ 1.52416, $n_\gamma^{16.35}$ 1.53376, n_D^{20} 1.5111. H. W.

Pyro-condensations in the Aromatic Series. HANS MEYER and ALICE HOFMANN (*Monatsh.*, 1916, **37**, 681—722).—The first of three papers on this subject, the second having already been reviewed in A., 1917, i, 641, and the third in A., 1918, i, 66. The object of the initial investigation was to study the products formed by the decomposition of the vapours of non-halogenated aromatic compounds at the lowest possible temperatures, the method being similar to that described in a series of papers by Löb (1901—1905).

Benzene begins to decompose into diphenyl at 650° (compare Smith and Lewcock, T., 1912, **101**, 1453).

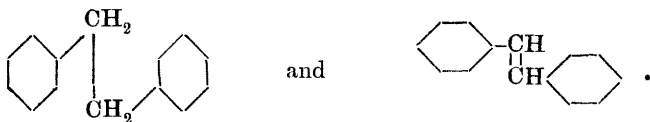
When kept for a few hours at a dull red heat, toluene vapour gives almost exclusively dibenzyl, the product which is formed when toluene is oxidised with potassium persulphate in the cold (Moritz and Wolfenstein, A., 1899, i, 424). At a bright red heat, however, hydrogen is also lost from the nucleus. The hydrocarbons which may be frozen out from the mixture at -80° include dibenzyl, stilbene, and anthracene (see below), whilst a study of the oxidation products of the remaining oil reveals the probable presence of di-*p*-tolyl and *p*-methyldiphenylmethane.

At a bright red heat, *p*-xylene readily yields *p*-dixylyl, $C_6H_4Me \cdot CH_2 \cdot CH_2 \cdot C_6H_4Me$, m. p. 81—82° (*ibid.*), but at a higher temperature (yellow heat) more oil is produced. The chief by-product is *pp'*-dimethylstilbene.

Mesitylene decomposes very smoothly, giving dimesityl.

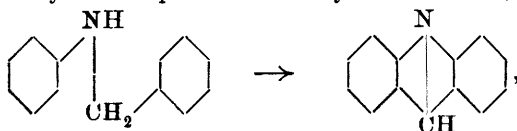
Ethylbenzene gives chiefly stilbene and an oily by-product, which only yields benzoic acid on oxidation, and therefore contains no hydrocarbons with condensed nuclei. The production of stilbene may be due to the elimination of methane and the union of the :CHPh residues, or to condensation to $\beta\gamma$ -diphenylbutane and loss of ethylene.

Dibenzyl gives stilbene and a very little toluene, with considerable quantities of anthracene, but no trace of phenanthrene. Stilbene, however, gives no anthracene or phenanthrene. This remarkable difference between dibenzyl and stilbene is explained by assuming that the positive methylene groups in the former bring the negative benzene nuclei close to the connecting chain, whereas the negative ethylene linking in stilbene keeps the nuclei at a distance, thus:

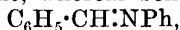


Several facts support this idea. In the first place, dihydroanthracene, which should be the primary product from dibenzyl, passes rapidly into anthracene at a red heat, and *p*-xylene or *p*-dixylyl gives 2:6-dimethylantracene at a bright red heat,

whereas mesitylene or dimesityl forms no anthracene derivative. Similarly, benzylaniline passes so readily into acridine,



that this pyrogenic method may be employed with advantage in the preparation of acridine, whereas benzyldeneaniline,



only yields aniline, benzonitrile, benzene, diphenyl, and such products.

Benzanilide gives a good yield of phenanthridone, m. p. 290° , which is reduced to phenanthridine by distillation over zinc dust.

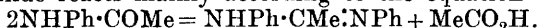
When diphenylmethane vapour is exposed to the glowing platinum spiral for seven hours, the products are benzene, toluene, a trace of diphenyl, and small quantities of anthracene, but chiefly fluorene, the process ranking as a convenient synthesis of this hydrocarbon. It is stated that Carnelley's " γ -methylenediphenyl" is only fluorene, and his " δ -methylenediphenyl" is most probably anthracene (T., 1880, **37**, 708).

Benzophenone is not easily changed, but the initial products are benzene and benzaldehyde.

Diphenyl ether readily yields diphenylene oxide, m. p. 81° .

Diphenylamine gives carbazole and some hydrogen cyanide, but di- α -naphthylamine loses ammonia and forms naphthalene instead of a substituted carbazole.

Acetanilide reacts mainly according to the equation



The bases are extracted from the ethereal solution of the product and then submitted to distillation in steam, when small quantities of aniline and *o*-aminoacetophenone (recognised by its jasmine-like odour) pass over, leaving a little *p*-aminoacetophenone and the diphenylethenylamidine behind.

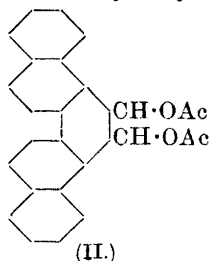
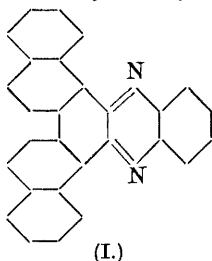
Naphthalene decomposes into $\beta\beta$ -dinaphthyl at a dull red heat, but as the temperature is raised more and more $\alpha\alpha$ -dinaphthyl is formed. The so-called $\alpha\beta$ -dinaphthyl (Smith, T., 1877, **32**, 559; Wegscheider, A., 1891, 216) is probably impure $\alpha\alpha$ -dinaphthyl.

Diphenyl gives 4:4'-diphenyldiphenyl, $\text{C}_6\text{H}_5\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_5$, m. p. 310° . *o-o'*-Ditolyl, from *o*-iodotoluene by heating with copper at 250° , reacts rapidly at the glowing spiral to form phenanthrene, which apparently gives diphenanthryl when the heating is continued. Anthracene gives 5:5'-dianthryl, but anthraquinone residues link up in the 2:2'-positions.

Weger reported the production of naphthalene by the passage of cyclopentadiene vapours through a red-hot tube (*Zeitsch. angew. Chem.*, 1909, **22**, 344), but this must have been due to the total disruption of the molecule and rebuilding from the ethylene and acetylene produced. Under the present conditions, no naphthalene

could be found, the products being partly evil-smelling oils and partly soluble or insoluble, but amorphous, solids.

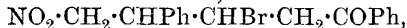
The so-called "Crackene" [with PAUL R. VON LENDENFELD].—Klaudy and Fink (A., 1900, i, 284) isolated "crackene" from the so-called red pitch formed in the "cracking" of oils, and suggested that it might be identical with "benzerythrene," since proved to be the above 4:4'-diphenyldiphenyl, but certainly not with picene. The present authors were struck with the fact that various fractions of the hydrocarbon varied slightly in colour. By treatment with a small quantity of bromine in warm chloroform, followed by repeated crystallisations from boiling xylene, they have succeeded in removing a coloured impurity and establishing the substance as picene. Picene may be characterised by conversion into picenequinone, and formation from this of *picenequinoxaline* (I), microscopic, yellow needles, by condensation with *o*-phenylenediamine. Picenequinone also forms a yellowish-brown *diacetyl* derivative (II), which may be hydrolysed to a dark dihydroxy-derivative.



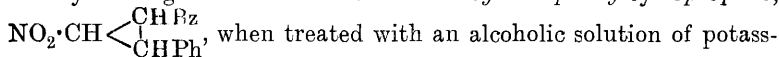
The acetylation is therefore accompanied by reduction. Picene and benzerythrene are said to dissolve in concentrated sulphuric acid with green colour. The pure hydrocarbons really give colourless solutions, picene exhibiting pale blue fluorescence.

J. C. W.

The cycloPropane Series. VII. Nitrocyclopropanes. E. P. KOHLER and H. F. ENGELBRECHT (*J. Amer. Chem. Soc.*, 1919, **41**, 1379—1384. Compare this vol., i, 533).—Phenyl styryl ketone condenses with nitromethane to form phenyl γ -nitro- β -phenylpropyl ketone, which yields two α -bromo-derivatives when treated with bromine in chloroform. The principal product has m. p. 100°, and is transformed into the isomeride, m. p. 106° (not 86°, as given in A., 1916, i, 404), by crystallising from an alcoholic solution of hydrogen bromide. The bromides,



readily change into 3-nitro-1-benzoyl-2-phenylcyclopropane,



ium acetate. The compound crystallises in clusters of stout prisms, m. p. 98°, and is changed by the action of hydrogen bromide dissolved in acetic acid into phenyl γ -bromo- β -nitro- γ -phenylpropyl ketone, $\text{CHPhBr} \cdot \text{CH}(\text{NO}_2) \cdot \text{CH}_2 \cdot \text{COPh}$, which forms colourless plates, m. p. 115—116°, and becomes yellow in sunlight. This

ketone is very sensitive. When boiled with methyl alcohol and a little ammonium bromide, for example, it changes into 2:5-diphenylfuran, and when heated above its m. p. it gives a pale yellow substance, plates, m. p. 77° , which is probably 3-bromo-1:5-diphenylfuran. The cyclopropane derivative reacts most readily with bases, but the products are complex mixtures. With sodium methoxide solution, under special conditions, it is possible to isolate $\alpha\delta$ -diphenylbutan- $\alpha\gamma$ -dione, $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{COPh}$. J. C. W.

Decomposition of Tetranitromethylaniline [2:4:6-Trinitrophenylmethylnitroamine]. EDMUND VON HERZ (*Z. ges. Schiess. u. Sprengstoffw.*, 1919, **14**, 155—157; from *Chem. Zentr.*, 1919, iv, 163).—The author's previous conclusion that the decomposition can be caused by electrolytic processes is confirmed by further laboratory experiments. Diazo-compounds similar to dinitrobenzoquinonediazide are probably formed, and not azide substances, such as $\text{O}:\text{C}_6\text{H}_2(\text{NO}_2)_2 < \begin{smallmatrix} \text{N} \\ | \\ \text{N} \end{smallmatrix}$. It is certain that the reactions

which result in the decomposition products affect the benzene nucleus exclusively; the occurrence of ammonia, methylamine, etc., is due solely to secondary changes, and has no influence on the characteristic transformation of the nucleus. The observed phenomena are not a specific property of tetryl, but are common to all trinitro-derivatives of benzene, such as trinitro-benzene, -toluene, -phenol, and -cresol. Decompositions of mercury fulminate in zinc capsules covered with an inner cap of copper or brass are probably also to be attributed to local electric currents. H. W.

Proteinogenous Amines. V. The Preparation of *p*-Hydroxyphenylethylamine Hydrochloride (Tyramine Hydrochloride). KARL K. KOESSLER and MILTON T. HANKE (*J. Biol. Chem.*, 1919, **39**, 585—592).—Certain improvements in the method for the synthesis of *p*-hydroxyphenylacetonitrile as given by Pschorr, Wolfes, and Buckow (*A.*, 1900, i, 170) are recorded. The reduction of this substance is effected by a method which it is claimed is more satisfactory than that employed by Barger (*T.*, 1909, **95**, 1127). The *p*-hydroxyphenylacetonitrile is dissolved in alcohol and treated with sodium, and after reduction is completed, the solution is rendered acid with hydrochloric acid. *p*-Cresol and *p*-hydroxyphenylacetic acid may then be removed by extraction with ether, after which the solution is rendered strongly alkaline and the tyramine is extracted with amyl alcohol. The amine may be extracted from the amyl alcohol by shaking with dilute hydrochloric acid. Yield, 58% of theoretical. The *p*-cresol and *p*-hydroxyphenylacetic acid present in the ethereal extract may be separated and isolated by shaking with sodium carbonate solution. The ethereal fraction retains the *p*-cresol, whilst the alkaline aqueous solution removes the *p*-hydroxyphenylacetic acid. J. C. D.

The Problem of the Physiological Polypeptide Synthesis. EMIL ABDERHALDEN and HANS SPINNER (*Zeitsch. physiol. Chem.*, 1919, **106**, 309—312).—By treating glycine with benzaldehyde in

absolute alcohol and sodium hydroxide, a condensation product identical with the benzylidene compound of *isodiphenyloxethylamine* is obtained in small needles, m. p. 132°. By treating glycine dissolved in sodium hydroxide with benzaldehyde and then oxidising with potassium permanganate, benzoic and hippuric acids are obtained.

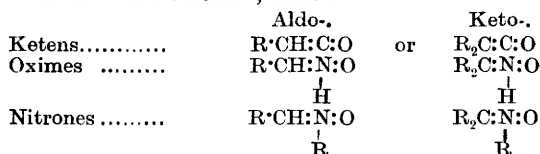
S. S. Z.

Dialkyl diaryl carbamides.

H. WINKEL (U.S. Pat. 1307570).—By conducting the reaction at 80—90°, diphenyldimethylcarbamide is prepared by passing carbonyl chloride directly into a mixture of methylaniline and dimethylaniline (which may also contain small quantities of aniline) without the use of a solvent. Aniline, methylaniline, and dimethylaniline may be mixed, in the proportions of 10, 40, and 50 parts respectively, and this mixture treated with carbonyl chloride until conversion of the methylaniline into diphenyldimethylcarbamide is completed as indicated by cessation of absorption of carbonyl chloride. The reaction mixture is then treated with dilute hydrochloric acid for the removal of dimethylaniline, and the product remaining is washed free from acid with water. It may then be further purified by crystallisation from any suitable solvent.

CHEMICAL ABSTRACTS.

Nitrones and Nitrenes. H. STAUDINGER and KARL MIESCHER (*Helv. Chim. Acta*, 1919, **2**, 554—582).—In connexion with his well-known studies of compounds with "twin bonds," Staudinger now describes several reactions of nitrones and a new class, the nitrenes. Nitrones are comparable in structure with the tautomeric forms of oximes and with ketens, thus:

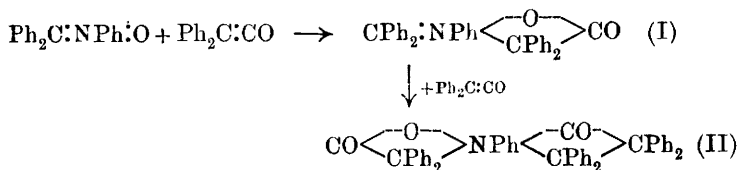


and nitrenes are comparable with allenes, thus: allenes, $R_2C:C:CR_2$; nitrenes, $R_2C:N:CR_2$. The simple nitrones are produced by the

alkylation of oximes, or by the action of aldehydes on *N*-substituted hydroxylamines. They are often formulated as cyclic ethers, thus, $R\cdot CH \begin{array}{c} \nearrow NR \\ \searrow O \end{array}$, although the evidence in favour of the nitrone formula

(the name was proposed by Pfeiffer, A., 1916, i, 327) has become very strong in recent years (compare Forster and Holmes, T., 1908, **93**, 244; Brady, T., 1914, **105**, 2104; Semper and Lichtenstadt, A., 1918, i, 437). It is now found that the "keto"-nitrones, $R_2C:NR:O$, are readily obtained by the action of aliphatic diazo-compounds on nitroso-compounds, the reaction being represented by the following scheme, although no intermediate products have been isolated: $R\cdot NO + R_2C \begin{array}{c} \nearrow N \\ \searrow N \end{array} \rightarrow RN \begin{array}{c} \nearrow O-N \\ \searrow CR_2 \end{array} \rightarrow RN \begin{array}{c} \nearrow O \\ \searrow CR_2 \end{array} \rightleftharpoons R_2C:NR:O$. The presence of two double linkings in these nitrones

is revealed by the fact that they combine with diphenylketen in two stages, thus:

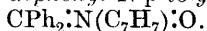


The nitrenes are formed when the products of the type I are heated, carbon dioxide being evolved. They are quite stable compounds, but capable of many reactions, of which combination with diphenylketen is particularly described.

Experiments with Diphenyldiazomethane.—Nitrosobenzene reacts with diphenyldiazomethane (A., 1916, i, 850) in ice-cold benzene to form diphenyl-*N*-phenylnitrene, $\text{CPh}_2:\text{NPh}:\text{O}$, which separates in pale yellow needles, m. p. 216—217° (decomp.) (Angeli, A., 1911, i, 544, gives m. p. 214°). The following reactions are described: (1) hydrolysis to benzophenone and *p*-aminophenol, by boiling with dilute sulphuric acid, thus: $\text{CPh}_2:\text{NPh}:\text{O} + \text{H}_2\text{O} \rightarrow \text{CPh}_2\text{O} + \text{OH}\cdot\text{NHPH} \rightarrow \text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$; (2) fission by means of hydroxylamine or phenylhydrazine, benzophenone-oxime or -phenylhydrazone being formed; (3) reduction to benzophenoneanil by heating with iron powder; (4) oxidation to benzophenone and nitrobenzene by ozonising and boiling the product with water; (5) decomposition on heating, either alone or with benzene at 250°, into benzophenone, benzophenoneanil, and nitrosobenzene. The nitrene combines with phenylcarbimide (1 mol.) in benzene to form a compound, $\text{C}_{26}\text{H}_{20}\text{O}_2\text{N}_2$, m. p. 164—165°, which loses carbon dioxide at 210° and is reconverted into the nitrene by boiling with alcohol. The reaction with diphenylketen in cold benzene, in an atmosphere of carbon dioxide, results in the formation of the above pale yellow compound (I), m. p. 181° (carbon dioxide evolved), the second compound (II), a white, crystalline powder, m. p. 166—168°, being formed if the reaction is carried out in boiling benzene.

Tetraphenyl-N-phenylnitrene, $\text{CPh}_2:\text{NPh}:\text{CPh}_2$, is formed by heating compound (I) at 190°. It crystallises in small, yellow prisms, m. p. 137°, and may be reduced by aluminium amalgam in ether to *dibenzhydrylaniline*, $\text{NPh}(\text{CHPh}_2)_2$, which crystallises in silvery needles, m. p. 160—161°, is so feebly basic that solutions in mineral acids deposit the base on dilution, and may be synthesised by heating together benzhydrylaniline, diphenylbromomethane, and quinoline. The nitrene combines with diphenylketen to form a compound, $\text{C}_{46}\text{H}_{35}\text{ON}$, white needles, m. p. 203·5—204·5°, and with hydrogen chloride to give a compound, $\text{C}_{32}\text{H}_{26}\text{NCl}$, m. p. 163°, both products yielding the nitrene again when heated.

[With E. SCHLENKER.]—Diphenyldiazomethane reacts with *p*-nitrosotoluene to give *diphenyl-N-p-tol'ylnitrene*,

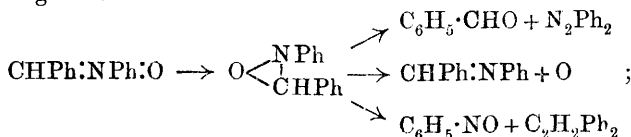


pale yellow needles, m. p. 153° (decomp.), which combines with

diphenylketen to form the compound, $\text{CPh}_2\text{:N}(\text{C}_7\text{H}_7)\text{<} \begin{smallmatrix} \text{O}\cdot\text{CO} \\ | \\ \text{CPh}_2 \end{smallmatrix}$, m. p. 161° , this decomposing at 170° into *tetraphenyl-N-p-tolyl-nitrene*, $\text{CPh}_2\text{:N}(\text{C}_7\text{H}_7)\text{:CPh}_2$, yellow crystals, m. p. 118° .

p-Nitrosodimethylaniline and diphenyldiazomethane produce *diphenyl-N-p-dimethylaminophenylnitrene*, $\text{CPh}_2\text{:N}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)\text{<} \begin{smallmatrix} \text{O}\cdot\text{CO} \\ | \\ \text{CPh}_2 \end{smallmatrix}$, as a pale yellowish-green powder, m. p. $186\text{--}187^\circ$ (decomp.). This gives a yellowish-green compound, $\text{C}_{35}\text{H}_{30}\text{O}_2\text{N}_2$, with diphenylketen, which decomposes at 169° into *tetraphenyl-N-p-dimethylaminophenylnitrene*, $\text{CPh}_2\text{:N}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)\text{:CPh}_2$, orange-yellow crystals, m. p. 155° .

Experiments with other Diazo-compounds.—Diphenylenediazomethane (*ibid.*) and nitrosobenzene produce *diphenylene-N-phenyl-nitrene*, $\begin{smallmatrix} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{>C:NPh:O}$, long, dark yellow needles, m. p. $192\text{--}193^\circ$ (decomp.), its diphenylketen compound, $\text{C}_{33}\text{H}_{23}\text{O}_2\text{N}$, pale yellow, m. p. $157\text{--}158^\circ$ (decomp.), and *diphenylenediphenyl-N-phenylnitrene*, $\begin{smallmatrix} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{>C:NPh:CPh}_2$, obtained as an impure, green powder, m. p. $90\text{--}100^\circ$. Phenyldiazomethane and nitrosobenzene give *phenyl-N-phenylnitrene*, CHPh:NPh:O , m. p. $112\text{--}113^\circ$, which is the product obtained by the interaction of benzaldehyde and phenylhydroxylamine. This nitrene decomposes when heated according to the scheme:



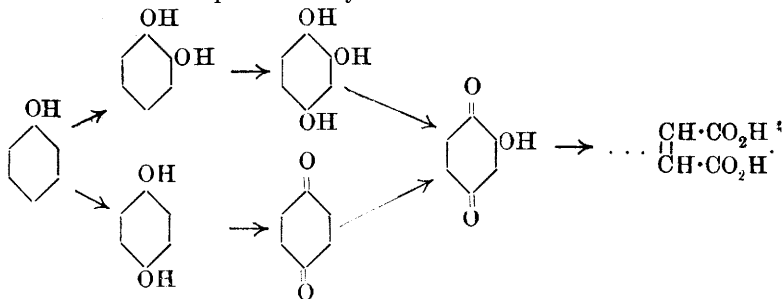
with the exception of the stilbene, all the products have been identified. The diphenylketen compound, $\text{CHPh:NPh}\text{<} \begin{smallmatrix} \text{O}\cdot\text{CO} \\ | \\ \text{CPh}_2 \end{smallmatrix}$, is a white powder, m. p. $186\text{--}190^\circ$, which decomposes on heating at 215° into *triphenyl-N-phenylnitrene*, CHPh:NPh:CPh_2 , pale yellow crystals, m. p. $105\text{--}106^\circ$, but also suffers rearrangement to a certain extent into a product, m. p. 223° , probably represented by the formula $\text{NPh}\text{<} \begin{smallmatrix} \text{CHPh}\cdot\text{CPh}_2 \\ | \\ \text{O} \text{---} \text{CO} \end{smallmatrix}$.

Ethyl diazoacetate and nitrosobenzene only react slowly and give a viscous, reddish-yellow oil, which decomposes on distillation in a vacuum into ethyl glyoxylate and azobenzene. J. C. W.

Electrochemical Oxidation of Phenols and Cresols.

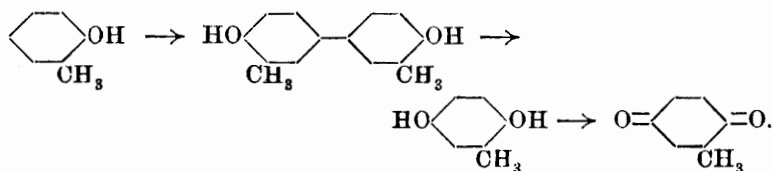
FR. FICHTER and FRANZ ACKERMANN (*Helv. Chim. Acta*, 1919, **2**, 583—599).—A continuation of previously published work on the electrochemical oxidation of phenol (Fichter and Stocker, A., 1914, i, 946). It has been shown that the electrochemical oxidation of phenol produces *op'*-diphenol and *pp'*-diphenol, which are inter-

mediate products in the formation of quinol and catechol. In the present experiments, 5.5 grams of catechol dissolved in 60 c.c. of 0.5*N*-sulphuric acid were subjected to a current of 0.02 amp./cm.² between lead electrodes. When no diaphragm was used, the products consisted of carbon dioxide, carbon monoxide, a volatile liquid with an odour of butyric acid, which consists of a mixture of butyric acid and its lower homologues, particularly formic acid, and succinic acid. When a diaphragm is used, the product consists of fumaric acid. The electrochemical oxidation of phenol to fumaric acid is represented by the scheme:

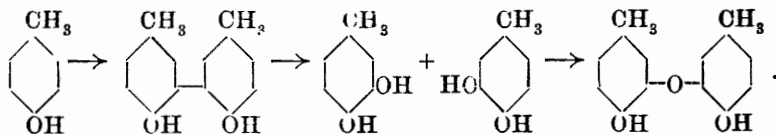


A number of experiments are described in which an attempt is made to ascertain the relative quantities of catechol and quinol produced in the electrochemical oxidation of phenol. By means of *E.M.F.* measurements, it is shown that at low concentrations quinol is a more active depolariser of a platinum electrode in 2*N*-sulphuric acid than catechol, but at concentrations above 0.05*N* the relationship is reversed. In a neutral solution, phenol has no depolarising action, and catechol has a much stronger depolarising action than quinol. In the case of a lead dioxide anode, catechol is much the strongest depolariser, so that the results allow no conclusion to be drawn as to the ratio of the two substances formed. An estimation of the amount of carbon dioxide formed in the electrolysis of phenol, catechol, and quinol, respectively, leads to the result that approximately the same quantities of quinol and catechol are formed in the electro-oxidation of phenol. An attempt to estimate directly the amount of quinol formed yielded no definite result, chiefly because of the presence of a resin in the products. The formation of the fatty acids is due to a reduction of the catechol, followed by an oxidation of the product of reduction. The reduction product of catechol is shown in a separate experiment to be *cyclohexanol*. This can be prepared by reducing a solution of 2.2 grams of catechol in 50 c.c. of 2*N*-sulphuric acid in a large platinum crucible with the anode in a porous pot. The high boiling residue of the electro-oxidation of phenol is shown to consist of diphenols, *o*-hydroxyphenyl ethers, diphenyl, tetrahydroxydiphenyl, and a dihydroxydiphenyl ether of the formula $\text{HO}\cdot\text{C}_{10}\text{H}_8\cdot\text{O}\cdot\text{C}_{12}\text{H}_8\cdot\text{OH}$. The electro-oxidation of *o*-cresol (540 grams in 2½ litres of *N*-sulphuric acid) by a current of anode density 0.0025 amp./sq. cm. without diaphragm and with vigorous

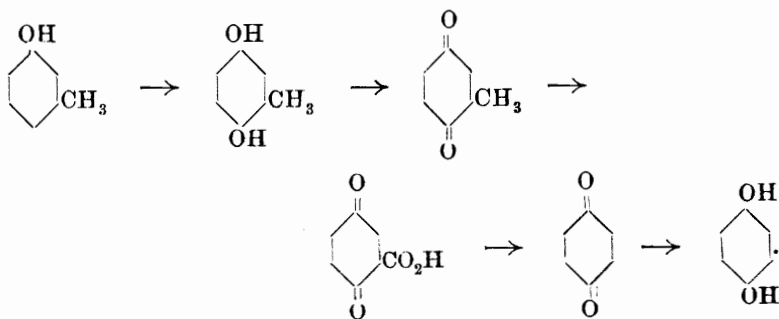
stirring gave, after 135.3 amp. hours had been passed, a dark brown oil and an aqueous solution. The oil consisted of *o*-dicresol, and the aqueous solution contained 2:5-toluquinone. The present results, together with previous work, show that the electro-oxidation of *o*-cresol may be represented by the scheme:



Similar experiments with *p*-cresol yielded from the aqueous layer toluquinone and benzoquinone, whilst the oily layer gave *p*-dicresol and 2:2'-dihydroxy-5:5'-dimethyldiphenyl ether. The formation of the latter compound is regarded as due to the loss of a molecule of water from two molecules of homocatechol. The electro-oxidation of *p*-cresol is represented by the scheme:



The formation of 2:5-toluquinone and *p*-benzoquinone in the present case is attributed to the presence of *m*-cresol in the material used. The oxidation scheme for *m*-cresol is represented as follows:



J. F. S.

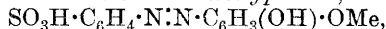
Certain Amino- and Acylamino-phenol Ethers. MICHAEL HEIDELBERGER and WALTER A. JACOBS (*J. Amer. Chem. Soc.*, 1919, **41**, 1450—1472).—DERIVATIVES OF PHENOL AND *o*- AND *m*-CRESOL.—Chloroaceto-*o*-anisidide, from the base by the method already described (*A.*, 1917, i, 552), has m. p. 48.5—49° (corr.). Chloroaceto-*m*-anisidide, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$, forms tufts of flat needles, m. p. 90.5—91° (corr.). Chloroaceto-*o*-phenetidide crystallises in hexagonal rhombs, m. p. 65.5—67.0° (corr.), and chloroaceto-*m*-phenetidide in glistening, flat needles, m. p.

125.5—126.5°. *Aceto-4-methoxy-m-toluidide*, large, nacreous scales, m. p. 103—103.5°, from 5-amino-*o*-cresol (A., 1917, i, 695) by acetylation and then methylation with methyl sulphate, is hydrolysed by boiling hydrochloric acid (1:1) to 4-methoxy-*m*-toluidine, m. p. 59—59.5° (Bamberger, A., 1912, i, 691), and then converted into *chloroaceto-4-methoxy-m-toluidide*, delicate needles, m. p. 90—92°. 4-Methoxy-*o*-toluidine, m. p. 13—14° (corr.), b. p. 146—147°/23 mm. (*ibid.*), is obtained by the methylation and subsequent hydrolysis of 6-acetylamino-*m*-cresol (A., 1917, i, 695), and converted into *chloroaceto-4-methoxy-o-toluidide*, which forms hair-like needles, m. p. 134.5—135.5°. 3-Nitro-*p*-anisidine, obtained by nitrating aceto-*p*-anisidide and hydrolysing the product, crystallises in orange-red prisms and plates, m. p. 57—57.5° (corr.), and 3-nitro-4-methoxychloroacetanilide forms golden-yellow, flat needles, m. p. 149.5—151.5°. *p*-Anisidine is sulphonated and then acetylated, yielding 3-acetyl-amino-6-methoxybenzenesulphonic acid, flat needles, which intumesce at 197—198°, then resolidify, and finally melt at 250° (decomp.). The crude sodium salt of this acid is ground with phosphorus pentachloride, and the product is converted into the *sulphonamide*, m. p. 233—235.5° (not purified), which is hydrolysed by dilute hydrochloric acid to 3-amino-6-methoxybenzenesulphonamide, radiate aggregates of creamy spindles, m. p. 184.5—186°.

DERIVATIVES OF THE ETHERS OF 4-AMINOCATECHOL.—3:4-Methylenedioxychloroacetanilide forms microscopic needles, m. p. 157.5—158.5°. 4-Aminoguaiacol (this vol., i, 265) yields 4-hydroxy-3-methoxychloroacetanilide in pale pink, nacreous plates, m. p. 113—114°. 3-Hydroxy-4-methoxychloroacetanilide also forms pale pink, nacreous plates, m. p. 140—150°. *o*-Ethoxyphenol is coupled with diazotised sulphanilic acid, and the dye, *p*-sulphobenzeneazo-ethoxyphenol, dark red plates with 2H₂O, is reduced by means of ammonium sulphide to 4-amino-6-ethoxyphenol (4-hydroxy-5-ethoxyaniline), which crystallises in minute, hexagonal plates, m. p. 186—188°. This base yields 4-hydroxy-5-ethoxyacetanilide, nacreous plates, m. p. 165.5—166.5°, and the *-chloroacetanilide*, OEt·C₆H₃(OH)·NH·CO·CH₂Cl, woolly needles, m. p. 155—156°. 3:4-Dimethoxychloroacetanilide, long, silky needles, m. p. 133.5—134.5°, is obtained from 4-aminoveratrole. 4-Acetylamino-guaiacol is ethylated by means of ethyl sulphate, giving 3-methoxy-4-ethoxyacetanilide, long, narrow, nacreous plates, m. p. 148.5—150° (Freyss's methoxyphenacetin?, A., 1901, i, 321). This is hydrolysed to 3-methoxy-4-ethoxyaniline, prismatic needles, m. p. 55° (corr.), b. p. 175—176°/20 mm., and then converted into the *chloroacetanilide*, long, silky needles, m. p. 133—134°. The above 4-hydroxy-5-ethoxyacetanilide is methylated and converted into 4-methoxy-5-ethoxyacetanilide, very thin, faintly purple scales, m. p. 145—146°, 4-methoxy-5-ethoxyaniline, faintly pink, rhombic crystals, m. p. 81.5—82° (corr.), and the *chloroacetanilide*, woolly needles, m. p. 135.5—136°. The same compound, on ethylation, yields 3:4-diethoxyacetanilide, m. p. 124—125.5° (Wisinger,

A., 1901, i, 205), from which 3:4-diethoxyaniline, creamy prisms, m. p. 47·5—48·5°, and 3:4-diethoxychloroacetanilide, m. p. 122·5—124·5°, may be obtained.

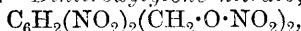
DERIVATIVES OF THE ETHERS OF RESORCINOL.—Resorcinol monomethyl ether is coupled with diazotised sulphanilic acid, and the dye, *p*-sulphobenzeneazo-*m*-methoxyphenol,



lustrous, brownish-orange platelets, with $1\text{H}_2\text{O}$, a brick-red powder, decomp. 250°, when dried, is reduced to 4-amino-5-methoxyphenol (4-hydroxy-6-methoxyaniline), pale purplish-brown needles, m. p. 175—180° (the hydrochloride is described by Henrich and Rhodius, A., 1902, i, 447). The base is converted into 4-hydroxy-6-methoxyacetanilide, pale pink aggregates of minute needles, m. p. 169—171·5°, and the chloroacetanilide, nacreous platelets, m. p. 165·5—166·5°. *p*-Sulphobenzeneazo-*m*-ethoxyphenol, flat, brownish-orange needles, with $1\text{H}_2\text{O}$, or a brick-red powder when dried, is obtained from resorcinol monoethyl ether and converted into 4-amino-5-ethoxyphenol (4-hydroxy-6-ethoxyaniline), grey, microscopic leaflets, m. p. 152—154°, 4-hydroxy-6-ethoxyacetanilide, pointed prisms, m. p. 172·5—174·5°, and the chloroacetanilide, feathery aggregates, m. p. 158·5—161°. 2:4-Dimethoxyaniline, m. p. 32·5—33·5°, is obtained from 4-hydroxy-2-methoxyacetanilide (compare Bechhold, A., 1889, 1155) and converted into 2:4-dimethoxychloroacetanilide, slender needles, m. p. 89·5—90° (corr.). The same compound is also ethylated, and thus made the source of 2-methoxy-4-ethoxyacetanilide, pale pink, glistening platelets, m. p. 117·5—118·5°, 2-methoxy-4-ethoxyaniline, faintly pink rhombs, m. p. 27·5—28·5° (corr.), b. p. 151·5—152·5°/12 mm., and the chloroacetanilide, flat, narrow, striated plates, m. p. 97·5—98°. The above 4-hydroxy-6-ethoxyacetanilide is methylated or ethylated, and converted in turn into 4-methoxy-6-ethoxyacetanilide, faintly pink, silky needles, m. p. 100·5—101°, 4-methoxy-6-ethoxyaniline, m. p. 22·5°, b. p. 144—144·5°, the chloroacetanilide, m. p. 126—127°, 2:4-diethoxyacetanilide, 2:4-diethoxyaniline, m. p. 33·5—34° (Will and Pukall, A., 1887, 660), and 2:4-diethoxychloroacetanilide, woolly needles, m. p. 102—103° respectively.

J. C. W.

Nitro-compounds for Use in Explosives. C. M. STINE (U.S. Pat. 1309551).—Dinitroxylylene nitrate,

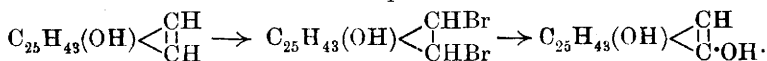


is produced by chlorinating xylene at 100° in sunlight until an increase in weight corresponding with the formation of the dichloro-derivative has been attained, cooling the reaction mixture to obtain a mass of crystals of *p*-xylylene chloride, and, after filtration, nitrating them with a mixture of nitric and sulphuric acids until a dinitro-derivative is obtained; this is heated with water under a pressure of 20 lb. per sq. in. until the chlorine has been replaced by the hydroxyl group, then evaporating the aqueous solution to expel water and hydrochloric acid, and obtain dinitro-*p*-xylylene hydroxide in well-defined crystals which are further nitrated. The

final product is a white, crystalline substance, which is stable and constitutes a powerful explosive. The following substances are also mentioned as capable of similar production and use: *dinitroxylyl nitrate*, *nitrohydroxyxylylene nitrate*, *dinitrohydroxyxylylene nitrate*, $\text{NO}_2 \cdot \text{C}_6\text{H}_2(\text{CH}_2 \cdot \text{O} \cdot \text{NO}_2)_3$, $\text{C}_6\text{HMe}(\text{NO}_2)_2(\text{CH}_2 \cdot \text{O} \cdot \text{NO}_2)_2$.

CHEMICAL ABSTRACTS.

Hydroxycholesterol. III. I. LIFSCHÜTZ (*Zeitsch. physiol. Chem.*, 1919, **106**, 271—296. Compare A., 1914, i, 683; 1916, i, 558).—Cholesterol dibromide, prepared by brominating cholesterol, gives up a part of its bromine on heating with acetic acid. The bromine is removed from the dibromide more readily by boiling with water. By boiling for some time in the presence of sodium acetate in a reflux condenser it may be removed entirely, giving rise to a mixture which is partly amorphous and partly crystalline. The spectrum analysis and other reactions show that the amorphous product is hydroxycholesterol, identical with the compound obtained by the oxidation of cholesterol. The formation of hydroxycholesterol from the dibromide of cholesterol is represented as follows:



The double bond of the cholesterol eliminated by the bromination is thus re-established.

The crystalline substance, m. p. 139—141°, is a modified cholesterol, for which the author proposes the name of *metacholesterol*. A similar substance is prepared directly from cholesterol by oxidation. Mineral acids have the same effect on cholesterol dibromide as water, only the reaction is more vigorous.

On boiling cholesterol dibromide with dilute aqueous potassium hydroxide, hydroxycholesterol as well as the unchanged dibromide is obtained. Alcoholic potash, on the other hand, produces a substance which shows the properties of a hydroxy-derivative of cholesterol, but is not identical in its properties with the known hydroxycholesterol. The author names this substance *isohydroxycholesterol*. Details are further given of the bromination of hydroxycholesterol.

S. S. Z.

Crystallography of Phenyl Benzoate. MARIA STURA (*Riv. Min. Crist. Ital.*, 1917, **48**, 86—90).—This compound is monoclinic; complete crystallographic data are given. CHEMICAL ABSTRACTS.

Action of Cyanogen Bromide on Aromatic Hydrocarbons under the Influence of Aluminium Chloride. P. KARRER and E. ZELLER (*Helv. Chim. Acta*, 1919, **2**, 482—486).—When aromatic hydrocarbons are mixed with finely powdered aluminium chloride and freshly prepared cyanogen bromide and subsequently warmed until evolution of halogen hydrides ceases, good yields of nitriles are obtained. Toluene gives *p*-toluonitrile with a very little of the *o*-nitrile, and anthracene, dissolved in carbon disulphide, gives the unknown *anthracene-9-carboxylonitrile*, m. p. 170—172°, which is

identified by hydrolysis to the known acid and oxidation to anthraquinone.

Scholl and Nörr obtained quite different results when investigating this reaction (A., 1900, i, 386). It may be that they did not use fresh cyanogen bromide, for this is essential to the production of nitriles.

J. C. W.

Preparation of Vanillin. CONFECTIONERY INGREDIENTS, LTD., FRANCIS EDWARD MATTHEWS, ALBERT THEODORE KING, and THOMAS KANE (Brit. Pat., 131161).—Acyl derivatives of 4-hydroxy-3-methoxybenzoyl chloride, such as the acetate, benzoate, or carbonic ester or the *p*-toluenesulphonic ester, and arylalkyl derivatives, such as the benzyl ether, are reduced to the corresponding vanillin derivatives when their solution in toluene, xylene, or other suitable inert solvent is subjected at boiling temperature to a current of dry hydrogen in presence of a suitable catalyst; this may consist of any metal ordinarily known to be suitable for carrying out hydrogenations or reductions in liquid media (although palladium is preferred), deposited if desired on asbestos or barium sulphate or other suitable carrier. The product of reduction is hydrolysed to vanillin. Thus a nearly theoretical yield of vanillin sodium hydrogen sulphite is obtained when dry hydrogen is passed through a boiling mixture of vanilloyl chloride *p*-toluenesulphonic ester (154 parts), dry xylene (1000 parts), and palladised barium sulphate (5%, 30 parts) until evolution of hydrogen chloride ceases.

H. W.

Benzaldoxime Peroxide. PAUL ROBIN (*Compt. rend.*, 1919, 169, 695—696).—Contrary to Beckmann's results (compare A., 1889, 980), the author finds that when benzaldoxime peroxide is boiled in benzene it decomposes, giving benzaldoxime and dibenzenyloxyazoxime. When oxidised by iodine and sodium carbonate the peroxide gives dibenzenyloxyazoxime and its decomposition products.

W. G.

Hydroxy-carbonyl Compounds. II. Synthetic Experiments in the Filix Group. P. KARRER (*Helv. Chim. Acta*, 1919, 2, 466—481. Compare this vol., i, 160).—The extract of male fern root (*Aspidium filix mas*), which is the favourite remedy against the tape-worm, contains a number of active principles which have been investigated by Boehm (A., 1898, i, 40; 1899, i, 32, 804; 1902, i, 36, 37). These are all butyryl derivatives of phloroglucinol ethers, aspidinol having one benzene nucleus, albaspidin and flavaspidic acid having the structure of diphenylmethane, and filixic acid that of triphenylmethane. With the exception of the alkaloids of the pomegranate root, all other known tænia drugs are also butyric or isobutyric acid derivatives. It is, therefore, of interest to synthesise simple butyrophenones in order to test their physiological action. In addition, many indications have been received that the activity of related substances is greater the fewer the number of methyl

groups which are present as substituents in the nuclei. For example, trypaflavine is more active than acridine-yellow, salvarsan than its dimethyl derivative, and cignolin than chrysarobin. Consequently, the aim in the present synthesis is to obtain butyrophenone derivatives with as few methyl groups as possible. Hoesch's method has again proved successful, the butyronitriles condensing quite readily with phloroglucinol derivatives in the presence of hydrogen chloride and zinc chloride.

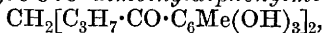
Phlorobutyrophenone [2:4:6-trihydroxyphenyl propyl ketone] crystallises in long needles with $1\text{H}_2\text{O}$, which lose water at 110° and then have m. p. $179\text{--}180^\circ$. It gives an intense red colour with ferric chloride, and couples with diazoaminobenzene to form 2:4:6-trihydroxy-3:5-dibenzeneazophenyl propyl ketone, in felted masses of orange-red needles, m. p. $136\text{--}137^\circ$. *Phloroisobutyrophenone* [2:4:6-trihydroxyphenyl isopropyl ketone] also crystallises with $1\text{H}_2\text{O}$ in white needles, m. p. $177\text{--}178^\circ$ (mixed m. p. 174°).

Methylphloroglucinol is prepared by dissolving phloroglucinol in water, adding hydrochloric acid and formalin, and reducing the precipitate of hexahydroxydiphenylmethane with zinc dust and sodium hydroxide. It reacts as above to form methylphlorobutyrophenone [2:4:6-trihydroxy-m-tolyl propyl ketone], which crystallises with $1\text{H}_2\text{O}$, m. p. $154\text{--}155^\circ$, and gives a violet colour with ferric chloride. Dimethylphloroglucinol yields dimethylphlorobutyrophenone (2:4:6-trihydroxy-m-5-xylyl propyl ketone), which is less soluble than the isomerides, crystallises in anhydrous, felted needles, m. p. 140° , and gives a dirty, yellowish-brown colour with ferric chloride.

Phloroglucinol monomethyl ether gives the two isomeric phlorobutyrophenone methyl ethers. One is more soluble in light petroleum and less soluble in water than the other, and these are sufficient reasons for supposing that this one has the ketone group opposite the methoxyl group, that is, it is 2:6-dihydroxy-4-methoxyphenyl propyl ketone; it crystallises in pale yellow leaflets, m. p. 113° . The isomeride, 2:4-dihydroxy-6-methoxyphenyl propyl ketone forms pure white needles, m. p. 130° .

Methylphloroglucinol *p*-methyl ether yields 2:4-dihydroxy-6-methoxy-m-tolyl propyl ketone, in white needles, m. p. $151\cdot5^\circ$. Aspidinol, m. p. $156\text{--}160^\circ$, is the 4:6-dihydroxy-2-methoxy-derivative, and therefore the synthetic ketone is designated *isoaspidinol*.

Methylphlorobutyrophenone condenses with formaldehyde in the presence of dilute sodium hydroxide to form 2:4:6:2':4':6'-hexahydroxy-5:5'-dibutyro-3:3'-dimethyldiphenylmethane,



which crystallises in microscopic needles, m. p. 212° . Phlorobutyrophenone and phloroisobutyrophenone also condense with formaldehyde to form such compounds, but owing to the free position in the nuclei, further condensations take place to a certain extent and the products are impure.

The naturally occurring filix compounds are more active the more complex they are, but of the above synthetic products the unicyclic ones are more active than the diphenylmethane representatives.

Phloro*isobutyrophenone*, which so closely resembles its isomeride in m. p. and chemical properties, has about twice its activity.

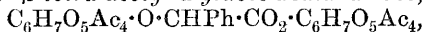
J. C. W.

Hydroxy-carbonyl Compounds. III. Synthesis of *isocotoin*. P. KARRER (*Helv. Chim. Acta*, 1919, 2, 486—489).—With the hope of synthesising *cotoin* (2:6-dihydroxy-4-methoxybenzophenone), the active ingredient of *coto-bark*, Hoesch's method has been applied to phloroglucinol monomethyl ether and benzonitrile. The only product which could be isolated, however, and this in good yield, is *isocotoin* [2:4-dihydroxy-6-methoxybenzophenone], which crystallises from water in yellow needles, m. p. 162° (*cotoin* has m. p. 131°). It seems to be the rule that ketones of this type, with the methoxyl group adjacent to the ketone group, are more soluble in water and less soluble in light petroleum than their isomerides with a *p*-methoxyl group [compare *paeonol* and *isopaeonol*, *acetoevernone* and *isoacetoevernone* (A., 1915, i, 820), and the phlorobutyrophenone methyl ethers (preceding abstract)].

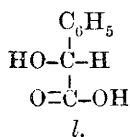
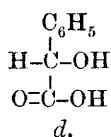
Piperonylonitrile forms a *double compound* with zinc chloride, $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CN}\cdot\text{ZnCl}_2$, which crystallises in slender needles, m. p. 157—158°, and therefore cannot be used in Hoesch's synthesis.

J. C. W.

Glucosides. IV. The Glucosides of Mandelic, Lactic, and Salicylic Acids. A New Chemical Resolution of Mandelic Acid. P. KARRER, C. NÄGELI, and H. WEIDMANN (*Helv. Chim. Acta*, 1919, 2, 425—436. Compare this vol., i, 338).—Besides the tetra-acetylglucosidomandelic acids and the tetra-acetylglucose mandelates which are formed when the silver salts of active and inactive mandelic acids are treated with acetobromoglucose, *l*-mandelic acid, and this isomeride only, gives a *tetra-acetyl-d-glucose β-tetra-acetyl-d-glucosidomandelate*,



in snowy crystals, m. p. 235°, $[\alpha]_D^{11} - 74\cdot96^\circ$ (in chloroform). A separation of the three products is effected as follows. The tetra-acetylglucosidomandelate remains in solution in the toluene on cooling the reaction mixture, whilst the new ester and the tetra-acetylglucose mandelate separate. The new ester is almost insoluble in alcohol, and may thus be freed from the tetra-acetylglucose mandelate. Starting with inactive mandelic acid, a clear separation of the active components may thus be effected. The different behaviour of the two acids may be explained on steric grounds; it is possible that in the *d*-acid the hydroxyl groups are so near together that there is only room for one tetra-acetylglucose residue at a time, thus:



If this is so, then inactive acetobromoglucose should effect the same separation, and the authors are collecting the necessary material for such an investigation.

More complete directions are given for the preparation, from the tetra-acetyl compounds, of β -*d*-glucosido-*d*- and -*l*-mandelic acids. These crystallise with 1EtOH in slender needles. β -*d*-Glucosido-*dl*-lactic acid, a hygroscopic, snowy powder, is also more completely described.

Tetra-acetyl-*d*-glucose salicylate has $[\alpha]_D^{16} - 39.50^\circ$ (in chloroform) and β -tetra-acetyl-*d*-glucosidosalicylic acid has $[\alpha]_D^{16} - 28.47^\circ$ (compare A., 1917, i, 539). The latter has now been hydrolysed to β -*d*-glucosidosalicylic acid, $C_6H_{11}O_5 \cdot O \cdot C_6H_4 \cdot CO_2H$, which crystallises in radiate bundles of needles with $1H_2O$, m. p. 142° (decomp.), $[\alpha]_D^{16} - 49.25^\circ$, and may be called *salicinic acid*, because of its relationship to salicin.

J. C. W.

A Simple Method of Demonstrating the Production of Aldehyde by Chlorophyll and by Aniline Dyes in the Presence of Sunlight. W. J. V. OSTERHOUT (*Amer. J. Bot.*, 1918, 5, 511—513).—For the preparation of chlorophyll for the experiments described, fresh leaves were extracted with alcohol, the alcoholic extract shaken with carbon tetrachloride, and the carbon tetrachloride, after separation, sprayed on to filter paper and allowed to evaporate. After spraying the paper several times, it acquired a deep green colour. A bell jar was lined with such filter paper, moistened with water, and then inverted over a small dish of water, sealed from the air and exposed to sunlight. When the paper was bleached to a pale green colour, the water in the dish generally gave a positive test for aldehydes, indicating the formation of a volatile aldehyde. The result was the same whether carbon dioxide was entirely excluded from the air in the jar or whether its concentration was increased to 10%. This supports the view that the aldehyde is not produced by the decomposition of carbon dioxide, but rather by the decomposition of the chlorophyll.

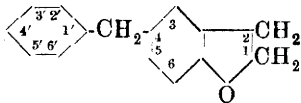
Similar results were obtained when a number of aniline dyes, particularly methyl-green and iodine-green, were used in place of chlorophyll.

W. G.

Syntheses in the Catechin Group. P. KARRER and FR. WIDMER (*Helv. Chim. Acta*, 1919, 2, 454—465).—Compounds of the type of catechin, $C_6H_3(OH)_2 \cdot CH(OH) \cdot C_6H(OH)_2$ $\leftarrow \begin{array}{c} CH_2 \cdot CH_2 \\ | \\ O \end{array}$,

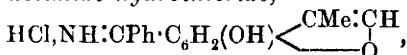
are widely distributed in nature, but the only syntheses which have been effected in this series are due to Kostanecki and his pupils; they are very complicated, and so far have only furnished methyl ethers of the desired products. A simple method has now been discovered. Hydroxycoumarones or hydroxycoumarans are condensed with nitriles under the influence of hydrogen chloride, and the ketimides so formed are boiled with water, giving ketones which are easily reduced to the required secondary alcohols. The method is, in effect, another application of Hoesch's synthesis of phenolic ketones (A., 1915, i, 820; 1917, i, 342).

It is proposed to call the parent 4-benzylcoumaran "depsan," and the coumarone derivative "depsen," with depsanone and depsenone for the ketones, and depsanol and depseanol for the secondary alcohols, the notation being as in the annexed formula.



Resorcinol and ethyl chloroacetate are condensed in the presence of sodium ethoxide to ethyl *m*-hydroxymethylcoumarilate, m. p. 178°, which is hydrolysed to the free acid, m. p. 226° (evolution of carbon dioxide). The dry acid is heated at 180—190°, when 5-hydroxy-2-methylcoumarone is obtained as a sublimate of white needles, m. p. 103°, which may be preserved for a long time. This mode of preparation is an improvement on that of Hantzsch (A., 1887, 262) or Pechmann (A., 1901, i, 211). The coumarone exhibits sky-blue fluorescence in alkaline solutions, and gives a brownish-red coloration with alcoholic ferric chloride, which changes to blue on diluting with water. By reduction with sodium and alcohol, it yields 5-hydroxy-2-methylcoumaran, $\text{OH} \cdot \text{C}_6\text{H}_3 < \begin{smallmatrix} \text{CHMe} \cdot \text{CH}_2 \\ \text{O} \end{smallmatrix}$, which sublimes or crystallises in white needles, m. p. 96°.

5-Hydroxy-2-methylcoumarone is dissolved in ether, mixed with a little zinc chloride and an equivalent quantity of benzonitrile, and the whole submitted to a current of dry hydrogen chloride for six hours. The *ketimide hydrochloride*,



which separates in bundles of pale green crystals, m. p. 77°, is boiled with water, and thus hydrolysed to 5-hydroxy-2-methyldepsenone (5-hydroxy-4-benzoyl-2-methylcoumarone). This crystallises in slender, golden-yellow forms, m. p. 158°, gives an intensely yellow sodium salt, and may be methylated by methyl sulphate. 5-Methoxy-2-methyldepsenone forms stout, pale yellow crystals, m. p. 79°, and does not reduce permanganate. This is important, as it shows that the furan ring of the original coumarone has not been ruptured during the condensation with the nitrile. Reduction of the ketone to the hydrol is effected by zinc dust and 5% sodium hydroxide. 5-Hydroxy-2-methyldepsenol forms bundles of small, very pale pink crystals, m. p. 141°.

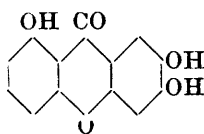
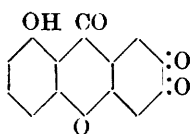
5-Hydroxy-2-methyldepsanone, small, sulphur-yellow needles, m. p. 159°, giving a green coloration with alcoholic ferric chloride, and 5-hydroxy-2-methyldepsanol, slender, pale pink needles, m. p. 152° (turns dark brownish-red at 100°), are obtained in the same way from 5-hydroxy-2-methylcoumaran.

J. C. W.

Correction of an Error Relating to a Trihydroxyxanthone.

A. L. VAN SCHERPENBERG (*Chem. Weekblad*, 1919, **16**, 1146—1149).—When euxanthone is oxidised with chromic acid, a red substance is obtained to which the constitution 2-hydroxy-5:8-quinoxanthone has been assigned (Nierenstein, A., 1913, ii, 382). Reduction of

this compound with zinc in acetic acid gives a yellow substance of the corresponding structure, 2:5:8-trihydroxyxanthone. The following arguments, based on the experimental results of Nierenstein, are advanced by the author against the adoption of this view. The red substance, on treatment with nitric acid, gives trinitroresorcinol, indicating the presence of a resorcinol residue not accounted for by the above formulation. Attempts to acetylate, benzoylate, and alkylate the quinone substance were not successful. This accords with the view that the hydroxyl group occupies the 8-position, and not the 3-position. The yellow reduction product melts with decomposition, a property of hydroxy-xanthenes with a hydroxyl group in the 3- or 6-position. The formulation of the two substances as 8-hydroxy-2:3-quinoxanthone and 2:3:8-trihydroxyxanthone, respectively, is therefore proposed.



W. S. M.

δ -Cinchonine and its Isomerides ; its Relations to Niquine.

E. LÉGER (*Compt. rend.*, 1919, **169**, 797—800).—By fractional crystallisation of its hydrochloride from alcohol, it is now shown that the δ -cinchonine previously described by Jungfleisch and Léger (compare A., 1894, i, 262) is really a mixture of two isomerides, which the author names α -cinchonhydrine and β -cinchonhydrine. These substances have respectively m. p. $144\cdot4^{\circ}$ and $155\cdot8^{\circ}$, $[\alpha]_D + 196\cdot8^{\circ}$ and $+ 106^{\circ}$ (in water with 2HCl), $[\alpha]_D + 139\cdot8^{\circ}$ and $+ 72\cdot16^{\circ}$ (in alcohol). These figures indicate that the δ -cinchonine described by Langer (compare A., 1901, i, 403) is identical with the α -cinchonhydrine now described. With each of these bases, acetic anhydride gives a diacetyl derivative, from which the original base can be regenerated unchanged.

When heated for twenty-four hours with 50% sulphuric acid, α -cinchonhydrine is converted into γ -cinchonhydrine, which has $[\alpha]_D + 140\cdot2^{\circ}$.

It is suggested that the cinchonhydrines bear the same relationship to cinchonine as niquine does to hydroquinine. W. G.

The Crystallography of Morphine and certain of its Derivatives. EDGAR T. WHERRY and ELIAS YANOVSKY (*J. Washington Acad. Sci.*, 1919, **9**, 505—513).—Attempts have been made to apply the optical-crystallographic method devised for the identification of the cinchona alkaloids (A., 1918, ii, 339) to the morphine group of alkaloids and the crystallographic and optical properties of a number of these have been studied. Owing to the ready solubility, however, of these substances in every immersion liquid approaching them in refractive index, the method is impracticable.

Morphine monohydrate, $C_{17}H_{19}O_3N \cdot H_2O$, was obtained in good crystals from methyl alcohol: rhombic bisphenoidal [$a:b:c=0.499:1.0.927$]; refractive indices, α 1.580, β 1.625, γ 1.645. D 1.32; M.V. 229.7.

Codeine (morphine methyl ester), $C_{18}H_{21}O_3N$, was crystallised from ethyl acetate: rhombic bisphenoidal [$a:b:c=0.931:1.0.509$]; double refraction positive, dispersion strong. D 1.32; M.V. 226.7.

Codeine monohydrate, $C_{18}H_{21}O_3N \cdot H_2O$, was crystallised from water and from aqueous methyl alcohol: rhombic, probably bisphenoidal [$a:b:c=0.960:1.0.830$]; double refraction negative, dispersion distinct. D 1.31; M.V. 242.1.

Codethyline (morphine ethyl ester monohydrate), $C_{19}H_{23}O_3N \cdot H_2O$, crystallised from ether in prisms: rhombic, probably bisphenoidal [$a:b:c=1.454:1.0.789$]; double refraction positive, dispersion distinct. D 1.29; M.V. 256.7.

Heroin (diacetylmorphine), $C_{21}H_{23}O_5N$, was obtained in excellent crystals from ethyl acetate: rhombic bisphenoidal [$a:b:c=0.8952:1.0.497$]; double refraction negative, dispersion strong. D 1.32; M.V. 279.7.

The relations between the topic parameters of the crystals are discussed.
E. H. R.

Addition Reactions and Ring Fission of certain Heterocyclic Compounds. SIEGFRIED SKRAUP (*Annalen*, 1919, 419, 1—92).—The behaviour of various heterocyclic compounds towards hydroxylamine has been investigated; the results are interpreted with the aid of Werner's theory of the varying affinity values of simple bonds.

Ethyl 2:4:6-trimethyldihydropyridine-3:5-dicarboxylate reacts with hydroxylamine hydrochloride in boiling absolute methyl alcoholic solution to yield ammonium chloride, ethyl 2:4:6-trimethylpyridine-3:5-dicarboxylate, and 4-ethylidenebis-3-methyl-5-isooxazolone, $O \begin{array}{c} \diagup \text{CO} \cdot \text{CH} \text{---} \text{CHMe} \text{---} \text{CH} \cdot \text{CO} \diagdown \\ \text{N} = \text{CMe} \quad \text{MeC} = \text{N} \end{array} O$, m. p. 156° (compare

Rabe, A., 1904, i, 509). The primary product of the action appears to be ethyl ethylidenebisacetoacetate, which then yields the isooxazolone on the one hand and the pyridine derivative on the other hand through the intermediate formation of a *N*-hydroxy ring compound. In support of this hypothesis, it is found that small quantities of ethyl trimethylpyridinedicarboxylate are formed by the action of hydroxylamine hydrochloride on ethyl ethylidenebisacetoacetate. Under similar conditions, ethyl 2:6-dimethyldihydropyridine-3:5-dicarboxylate yields ethyl 2:6-dimethylpyridine-3:5-dicarboxylate in 20% yield, whilst a 49.5% yield of ethyl 4-phenyl-2:6-dimethylpyridinedicarboxylate, m. p. 66° (*picrate*, m. p. 148—149°), is obtained from the corresponding dihydro-compound. With ethyl 2:6-dimethylisopropylidihydropyridinedicarboxylate and ethyl 4-benzyl-2:6-dimethyldihydropyridinedicarboxylate a different but not unexpected behaviour is observed, since in each case the substituting group is eliminated and ethyl 2:6-dimethylpyridinedicarboxylate is produced.

Ethyl 2:5-dimethylpyrrole-3:4-dicarboxylate only reacts very slowly with hydroxylamine hydrochloride. The transformation of the dihydro-derivatives into the pyridine compounds can scarcely be ascribed to a direct oxidising action of hydroxylamine since, though these substances are readily oxidised by such agents as nitrous acid, sulphur, nitric and chromic acids, they are very resistant to iodine, ferric chloride in acetone solution, and to a large excess of permanganate.

A rigid proof of the relationship of dimethyldihydropyridine- and trimethyldihydropyridine-dicarboxylic esters to 1:4-dihydropyridine has not previously been given; attempts to identify the presence of an imino-hydrogen atom by acetylation were unsuccessful, but its presence could be shown with the help of magnesium methyl iodide.

Benzothiazole is transformed by hydroxylamine into 2-aminobenzothiazole, the yield being nearly quantitative; similarly, benzoxazole is converted into 2-aminobenzoxazole, m. p. 129—130°, and *o*-formylaminophenol (identified as dibenzoyl-*o*-aminophenol, m. p. 182—183°). The following substances do not react with hydroxylamine: benziminazole (the *picrate*, m. p. 225—226°; *copper salt*, $(C_7H_5N_2)_2Cu$, red precipitate; *nickel*, *cobalt*, *cadmium*, and *zinc* compounds are described); 1-methylbenziminazole (m. p. 66°, b. p. 286°/746 mm., conveniently prepared by the action of potassium methyl sulphate on sodium benziminazole in aqueous solution; *picrate*, m. p. 246—247°); 1-phenylbenziminazole, benzylidene-aniline, azobenzene, 1-phenylpyrazole, 2-phenyl-1:2:3-triazole, pyridine, quinoline, 2-methylbenzothiazole, 2-phenylbenzothiazole, 4:5-diphenyloxazole, 6-dimethylaminobenzothiazole.

The following 2-substituted benzoxazoles have been prepared by heating *o*-aminophenol with the requisite nitrile or amide: 2-*isobutylbenzoxazole*, almost colourless oil, b. p. 240°/748 mm., D_{17}^{20} 0.98; 2-*tert.-butylbenzoxazole*, colourless oil, b. p. 226°/748 mm., D_{17}^{20} 0.9466; 2-*n*-hexylbenzoxazole, b. p. 282—285°, m. p. 19°, D_{17}^{20} 0.944; 2-*cyclohexylbenzoxazole*, colourless crystals, m. p. 37—38°, b. p. 298°/744 mm.; 2-*benzylbenzoxazole*, pale yellow, viscous liquid, b. p. 325°/750 mm., D_{17}^{20} 1.113; 2-phenylbenzoxazole, non-fluorescent crystals, m. p. 103°; 2-*p*-tolylbenzoxazole, colourless needles, m. p. 116—117°; 2-*p*-anisylbenzoxazole, almost colourless, crystalline needles, m. p. 101°, b. p. 363°/742 mm.; 2- α -naphthylbenzoxazole, colourless crystals, m. p. 107°; 2-*p*-chlorophenylbenzoxazole, long, shining needles, m. p. 150°; 2-*p*-bromophenylbenzoxazole, m. p. 158—159°; 2-*styrylbenzoxazole* (?). The fission of the oxazole ring by aqueous hydrochloric acid has been studied, and reaction is shown to occur with decreasing rapidity when the substituents are arranged in the following order: benzyl, methyl, *n*-hexyl, cyclohexyl, *isobutyl*, *tert*.-butyl, phenyl, *p*-tolyl, α -naphthyl, *p*-anisyl. The results are fully discussed in the light of the theory of partial valency.

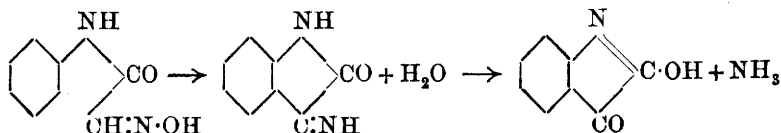
H. W.

Preparation of Isatin and its Substitution Derivatives and Intermediate Products. J. R. GEIGY (Brit. Pat. 128122).—The preparation of oximinoacetanilide and its substitution products

*b b**

is effected by subjecting aniline or its derivatives which are substituted in the benzene nucleus by halogens, alkyl, alkoxy, or carboxyl groups or the *N*-monoalkyl or *N*-monoaralkyl derivatives of these amines to the action of chloral hydrate in a dilute solution of a mineral acid and in the presence of hydroxylamine at a suitable temperature. Isatin and its substitution derivatives are obtained from oximinoacetanilide and its derivatives by treatment of the latter with concentrated sulphuric acid and afterwards splitting the resulting isatinimides by addition of water into isatins and ammonia. Reactions occur in accordance with the schemes

$$\text{CCl}_3 \cdot \text{CH}(\text{OH})_2 + \text{NH}_2 \cdot \text{OH} = \text{CCl}_3 \cdot \text{CH} \cdot \text{N} \cdot \text{OH} + 2\text{H}_2\text{O};$$

$$\text{CCl}_3 \cdot \text{CH} \cdot \text{N} \cdot \text{OH} + \text{C}_6\text{H}_5 \cdot \text{NH}_2 + \text{H}_2\text{O} = \text{NHPh} \cdot \text{CO} \cdot \text{CH} \cdot \text{N} \cdot \text{OH} + 3\text{HCl}.$$


Oximino-derivatives of the following amines have been prepared, the m. p.'s of the compounds being placed within brackets: *o*-toluidine (121°), *m*-toluidine (146°), *p*-toluidine (162°), *m*-xylylidine (161°), *p*-xylylidine (151°), methylaniline (145°), ethylaniline (160°), benzylaniline (142°), *o*-anisidine (140°), *p*-phenetidine (195°), anthranilic acid (208°), *o*-chloroaniline (150°), *m*-chloroaniline (154°), 2:5-dichloroaniline (163°), 3:4-dichloroaniline (158°), 3:5-dichloroaniline (185°), 5-chloro-*o*-toluidine (167°), 4-chloro-*o*-toluidine (148°), 6-chloro-*m*-toluidine (187°), 4-chloro-*m*-toluidine (134°), 2-chloro-*p*-toluidine (177°), 3-chloro-*p*-toluidine (188°), and *p*-bromoaniline (167°). The following isatins are described: mixture of 4- and 6-methylisatins, orange-yellow crystals, m. p. 143°; 4:7-dimethylisatin, orange-yellow crystals, m. p. 250°; 5:7-dimethylisatin, brick-red crystals, m. p. 235°; mixture of 4- and 6-chloroisatins, orange-yellow crystals, m. p. 212°; 7-chloroisatin, reddish-brown crystals, m. p. 175°; mixture of 4:5- and 5:6-dichloroisatins, yellowish-red crystals, m. p. 200°; 4:6-dichloroisatin, lemon-yellow crystals, m. p. 250°; 4-chloro-7-methylisatin, orange-yellow crystals, m. p. 273°; 5-chloro-7-methylisatin, yellowish-brown crystals, m. p. 265°; 7-chloro-4-methylisatin, orange-yellow crystals, m. p. 252°; mixture of 5-chloro-4-methyl- and 5-chloro-6-methylisatins, orange-yellow crystals, m. p. 200°; mixture of 4-chloro-5-methyl- and 6-chloro-5-methylisatin, bright red crystals, m. p. 205°; isatin-7-carboxylic acid, brownish-yellow powder, m. p. 235°. H. W.

Manufacture of *N*-Arylthiomorpholines. ROBERT ROBINSON, FRANCIS WILLIAM KAY, and BRITISH DYES, LTD. (Brit. Pat. 133108).—*N*-Arylthiomorpholines (*N*-arylthiazans) of the general formula $\text{Ar} \cdot \text{N} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{S}$, applicable as intermediate products in the manufacture of dyes, may be prepared by condensing primary aromatic amines, provided they are not substituted in the ortho-position, with $\beta\beta'$ -dichloroethyl sulphide. Suitable sol-

vents, such as toluene or nitrobenzene, may be employed, and also some agent capable of neutralising hydrogen chloride, such as sodium carbonate or acetate. In some cases, as in the reaction with β -naphthylamine, copper powder may be added with advantage. A less suitable method consists in heating the base and its hydrochloride with $\beta\beta'$ -dihydroxyethyl sulphide. *N*-Phenylthiomorpholine forms flat, elongated prisms, m. p. 32° , b. p. $200^\circ/50$ mm., has an alliaceous odour, and yields a *picrate*, m. p. 144° . *N*-*p*-Tolylthiomorpholine has m. p. 35° , and the β -naphthyl derivative has m. p. about 155° . J. C. W.

Ureides of Substituted Aminonaphtholsulphonic Acids.

B. HEYMANN, O. DRESSEL, R. KOTHE, and A. OSSENBECK (U.S. Pat. 1308071).—Ureides are produced having the general formula $\text{CO}(\text{NH}\cdot\text{C}_6\text{H}_m\text{Y}_4 - m\cdot\text{R}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_n\text{X}_6 - n\cdot\text{OH})_2$, in which R stands for a bivalent group containing an acyl radicle, for example, CO, SO_2 , $\text{CO}\cdot\text{CH}:\text{CH}$, $\text{CO}\cdot\text{CH}_2$, or the residue of phenylacetic acid; n is the number of hydrogen atoms remaining unsubstituted in the naphthalene ring; X is a sulphonic acid or other substituting group; m the number of unsubstituted hydrogen atoms in the benzene nucleus; and Y, substituting atoms or radicles, such as Cl, Br, Me, or OMe. These compounds form dyes when coupled with diazotised aniline or similar components, and may be employed as therapeutic agents for destroying blood-parasites. They form salts with alkali metals, alkaline earth metals, or heavy metals, for example, sodium, barium, strontium, copper, zinc, mercury, and silver, which also possess therapeutic properties. As starting materials, 1:8-aminonaphtholsulphonic acids (mono-, di-, or higher sulphonic acids) may be employed. These compounds are substituted by such nitro-compounds as *p*-nitrobenzoyl chloride, *m*-nitroanisoyl chloride, *m*-nitrobenzenesulphonyl chloride, or *m*-nitrocinnamoyl chloride. Reduction of these substituted aminonaphtholsulphonic acids is effected by the action of iron and acetic acid or other similar reducing agents, and the amino-compounds thus obtained are treated with carbonyl chloride to obtain ureides. CHEMICAL ABSTRACTS.

Hydrazino-acids. III. AUGUST DARAPSKY (*J. pr. Chem.*, 1919, [ii], **99**, 179—231. Compare A., 1918, i, 506, 553).—The hydrazino-acids described previously have been optically inactive; the author now describes the preparation of the optically active α -hydrazinophenylacetic acids, which are prepared by the action of hydrazine hydrate on the active phenylchloroacetic acids or by the resolution of α -benzylidenehydrazinophenylacetic acid and subsequent elimination of the benzylidene group. The applicability of these acids to the study of the phenomena of the Walden inversion is limited by their tendency to complete racemisation under the experimental conditions adopted.

d- and *l*-Phenylchloroacetic acids are prepared by the resolution of the *r*-acid by means of morphine according to the method of McKenzie and Clough (T., 1908, **93**, 817; 1909, **95**, 782), and their properties agree completely with those given by these authors; the unusual experimental difficulties encountered in this resolution have

been extensively investigated, the main factors conditioning success appearing to be the slowness with which the crystals of the salt separate and the relative weight of the crop which is deposited before filtration. *d-Hydrazinophenylacetic acid* is obtained by the action of hydrazine hydrate on *l*-phenylchloroacetic acid in absolute alcoholic solution; it crystallises in shining leaflets, m. p. 183—184°, and has $[\alpha]_D^{20} + 158.02^\circ$ in *N*-hydrochloric acid solution; *l-hydrazinophenylacetic acid*, m. p. 183—184°, $[\alpha]_D^{20} - 157.64^\circ$, is similarly prepared from the *d*-chloro-acid. The acids readily condense with benzaldehyde in aqueous solution in the presence of hydrochloric acid, yielding respectively *d*- and *l*-benzylidenehydrazinophenylacetic acids, m. p. 136—138°, $[\alpha]_D^{20} + 166.40^\circ$ and -166.59° in acetone solution.

The resolution of α -hydrazinophenylacetic acid into its active components cannot be conveniently effected by means of helicine or camphor, but may be accomplished if the acidic character of the substance is increased by the introduction of suitable groups; the formyl and benzoyl groups are not applicable, since viscous syrups are formed in the first instance and difficultly decomposable compounds in the second. The benzylidene derivative can, however, be resolved by morphine in alcoholic solution. (The crystalline quinine salts of *dl*-benzylidenehydrazinophenylacetic, *dl*-*o*-hydroxybenzylidenehydrazinophenylacetic and *dl*-*p*-methoxybenzylidenehydrazinophenylacetic acids, m. p.'s 172—174°, 183°, and 161—163° respectively, are described, but are not suited for the resolution; *dl*-*p*-methoxybenzylidenehydrazinophenylacetic acid forms small, colourless needles, m. p. 131—133°.) The physical properties of the *d*-acid obtained in this manner agree completely with those of the substance prepared by the action of hydrazine hydrate on *l*-phenylchloroacetic acid and treatment of the product with benzaldehyde.

Ethyl d- and *l*-hydrazinophenylacetate hydrochlorides, prepared by the esterification of the corresponding acids with alcohol and hydrogen chloride, have m. p. 148—150°, $[\alpha]_D^{20} + 96.32^\circ$ and -96.30° respectively. They are converted by nitrous acid into the corresponding nitroso-esters of the same sign, but considerable racemisation occurs which appears to be attributable to the nitrous acid; this is the more remarkable since a group directly attached to the asymmetric carbon atom is not involved in the change; further extensive racemisation takes place when the crude nitroso-esters are crystallised from alcohol. On the other hand, the conversion of nitroso- into azido-ester by treatment with dilute sulphuric acid appears to occur without racemisation, and yields a product of the same sign, but it is not possible to guarantee the optical purity of these substances. When the active nitroso-esters are heated they are converted into ethyl *dl*-aminophenylacetate, racemisation being complete.

dl-Azidophenylacetic acid, m. p. 98—101° (Forster and Müller, T., 1910, **97**, 138, give 98.5°), is conveniently prepared by the action of sodium azide on *r*-phenyl-chloro- or -bromo-acetic acid; when the reaction is applied to *d*-phenylchloroacetic acid, a levorotatory azido-acid is obtained, which, however, is not free from mandelic acid.

Attempts to resolve *dl*-azidophenylacetic acid by quinine, quinidine, or cinchonine were unsuccessful, but partial success was attained with brucine or morphine, but the specific rotations of the acids were so low that, although the results are concordant among themselves, it is probable that the resolution was incomplete. Esterification of the azido-acids showed that racemisation unexpectedly occurs during the process, the phenomenon being more marked with alcohol and sulphuric acid than with diazoethane. Similar instances of racemisation were encountered with the active phenylchloroacetic acids, but, in these cases, the more marked effect was caused by diazoethane. Ethyl *d*-phenylchloroacetate has b. p. $138^{\circ}/19$ mm., $[\alpha]_D^{20} + 121.05^{\circ}$ in alcoholic solution, but is possibly not quite free from the racemic substance. The values observed for the *l*-isomeride were b. p. $136^{\circ}/13$ mm., $[\alpha]_D^{20} - 108.45^{\circ}$.

d-Hydrazinophenylacetic acid is converted by chlorine into *r*-phenylchloroacetic acid; similarly, ethyl *l*-hydrazinophenylacetate hydrochloride is transformed into slightly laevorotatory ethyl phenylchloroacetate, which is not quite pure analytically. H. W.

Cause of and Remedy for certain Inaccuracies in Hausmann's Nitrogen Distribution Method. S. L. JODIDI and S. C. MOULTON (*J. Amer. Chem. Soc.*, 1919, **41**, 1526—1531).—The distribution of nitrogen in casein, gelatin, and egg-albumin has been investigated. It is shown that the proportion of amide nitrogen obtained by Hausmann's method as modified by Osborne and Harris (A., 1903, i, 585) is constant, and does not depend on the quantity of magnesia added to the distillation mixture. The percentage of nitrogen contained in the magnesium oxide precipitate is higher the greater the quantity of magnesium oxide employed in distillation. Conversely, the proportion of monoamino- and diamino-nitrogen is the smaller the larger the amount of magnesia used in distillation. In order to obtain uniform results and a minimum of "humin" nitrogen it is necessary to use the least possible amount of magnesia which is sufficient to render the substance to be distilled alkaline. In the case of plant and animal materials the uniform application of 1 gram of magnesia is satisfactory, whilst in the case of proteins 0.5 gram is sufficient. J. F. S.

Identity of Hordein and Bynin. HEINRICH LÜERS (*Biochem. Zeitsch.*, 1919, **96**, 117—133).—Hordein and bynin were submitted to an analysis by the Van Slyke method, and the results obtained from the two proteins were almost identical. The author, therefore, does not agree with Osborne that bynin, which is obtained from malt, is a different protein from the hordein of barley.

S. S. Z.

Guanylic Acid, its Preparation and Precipitability. R. FEULGEN (*Zeitsch. physiol. Chem.*, 1919, **106**, 249—259).—By treating nucleoprotein from the pancreas of cattle with sodium hydroxide and precipitating with 90% alcohol in the presence of ammonium chloride, the sodium salts of guanylic and another

nucleic acid are obtained. After the purification of this mixture, sodium guanylate is obtained by precipitation with sodium acetate in the cold. Sodium hydrogen guanylate, $C_{10}H_{18}O_8N_5PNa$, is prepared by dissolving the latter in ten parts of hot water and one part of glacial acetic acid, and precipitating, after quick cooling, with three volumes of alcohol. S. S. Z.

Urease and the Radiation Theory of Enzyme Action. I. and II. H. P. BARENDRECHT (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 1126—1142, 1307—1322).—After a criticism of the hypothesis put forward by Van Slyke (*A.*, 1914, **i**, 1181), the author puts forward a new hypothesis to explain enzyme action. An enzyme acts by radiation, and the enzyme particle contains the same molecule, which is liberated or acted on by this enzyme, in some active state. The radiation by which enzymes exert their action is due to the electrons forming part of the atoms, and is of the nature of electromagnetic induction. The radiation, by which urease acts on urea, originates from the enzyme molecule, and is able to exert its hydrolytic effect to a certain distance, probably very small. When the urease radiation strikes an urea molecule, it is absorbed. The amount of urea hydrolysed in unit time by an enzyme molecule would therefore be independent of the urea concentration if the other constituents of the solution had no power of absorption of this radiation. In addition to urea, the hydrogen ions are the only constituent which absorb the radiation in this hydrolysis. At constant temperature and constant hydrogen-ion concentration, the velocity of the reaction is given by $-dx = m(x/[x + nc]) \cdot dt$, in which x is the concentration of urea, c the concentration of hydrogen ions, and n the absorption coefficient of hydrogen ions, that of urea being taken as unity. The velocity constant m for a given temperature and H^+ ion concentration is proportional to the enzyme concentration only. If a is the initial urea concentration and $(a - x)/a = y$, then, after integration, $nc/0.434 \cdot \log(1/[1 - y]) + ay = mt$. This theory is tested by experiments made on the hydrolysis of urea by extract of soja beans, and the theory generally confirmed.

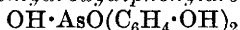
In the second paper, the work is repeated, but more precautions are taken to keep the hydrogen-ion concentration constant. It is found that the value of the constant m falls off towards the end of the reaction the higher the value of P_H . For low values of P_H , the value of m increases continually from 0.03% up to 8% urea concentration. For higher values of P_H , there is first an increase and then in the most concentrated solutions of urea a decrease in the value of m . These facts are deducible from the hypothesis formulated. J. F. S.

The Isomeric Hydroxyphenylarsinic Acids and the Direct Arsenation of Phenol. WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Amer. Chem. Soc.*, 1919, **41**, 1440—1450).—By means of the diazo-reaction, *o*- and *m*-arsanilic acids (this vol., **i**, 50) have been converted into the phenolic acids. *o*-Hydroxyphenylarsinic

acid, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{AsO}_3\text{H}_2$, crystallises readily from hot water, being but sparingly soluble in the cold, forming rosettes of needles, m. p. 196° , and its sodium salt, $\text{C}_6\text{H}_5\text{O}_4\text{AsNa}$, separates from 50% alcohol in glistening, hexagonal platelets with $4\text{H}_2\text{O}$. *m-Hydroxyphenylarsinic acid* crystallises from a small volume of water in masses of rhombs, m. p. $159\text{--}173^\circ$, and its sodium salt, rosettes of flat needles, is extremely soluble, even in alcohol. The ortho-acid differs from its isomerides in giving a wine-red colour with ferric chloride.

A knowledge of the *o*-hydroxyphenylarsinic acid has helped in the examination of the by-products formed in the arsenation of phenol. This important reaction is carried out as follows. Arsenic acid (480 grams of 80% acid), dehydrated by heating until the temperature reaches 150° , is mixed with phenol (200) and kept gently boiling at $155\text{--}160^\circ$ for seven hours. The homogeneous product is then diluted with water (2 litres), and sufficient of a hot concentrated solution of barium hydroxide is added to render the well-stirred mixture neutral to litmus. The precipitate of barium arsenate carries with it the small amount of tarry by-product. The hot filtrate is then treated with just sufficient sulphuric acid to precipitate the barium, filtered again, and the solution evaporated under reduced pressure to about half the volume, when it is neutralised by sodium hydroxide and concentrated to a small bulk. The hot solution is mixed with several volumes of alcohol and cooled, crystallisation being induced by rubbing. Using the quantities mentioned, about 120 grams of pure sodium *p*-hydroxyphenylarsinate are obtained, without the complications of Conant's method (this vol., i, 230).

The mother liquors, when the alcohol is removed by evaporation, give the above wine-red coloration with ferric chloride. Taking advantage of the different solubilities of the barium salts and the free acids, the authors have isolated *o*-hydroxyphenylarsinic acid (14 grams), Benda's *pp'*-dihydroxydiphenylarsinic acid, m. p. $250\text{--}251^\circ$ (10 grams; A., 1908, i, 747), and an acid which is probably *op'*-dihydroxydiphenylarsinic acid,



(8 grams). The latter acid crystallises from 50% acetic acid in stout, glistening prisms, m. p. $215\text{--}217^\circ$, and gives the red colour with ferric chloride.

J. C. W.

Physiological Chemistry.

Some Conditions Influencing the Reaction Velocity of Sodium Nitrite on Blood. C. R. MARSHALL (*Proc. Roy. Soc. Edin.*, 1918—1919, **39**, 149—156).—The rate of production of methæmoglobin by the action of sodium nitrite on blood is governed

by the nature and concentration of the blood solution and by the concentration of the sodium nitrite solution. Probably other factors, such as temperature, are of importance. J. C. D.

The Rôle of the Plasma Proteins in Diffusion. THOMAS HUGH MILROY and JOSEPH FRANCIS DONEGAN (*Biochem. J.*, 1919, **13**, 258—271).—After severe hæmorrhage, the specific gravity, viscosity, and percentage of nitrogen in the blood fall, whilst the conductivity rises. The fluid which enters the blood after hæmorrhage must have at least the electrolyte concentration of normal plasma, since there is no evidence of a fall in conductivity. It is evident from studies of diffusion of sodium chloride from solution in water, gum arabic solution, and blood serum that some factor other than viscosity is concerned in the diffusion of salt from serum. This point was studied further, and it is concluded from the results that the globulin may exert a determining factor governing the rate of diffusion. J. C. D.

Precipitation Structures Simulating Organic Growth. II. Physico-chemical Analysis of Growth and Heredity. R. S. LILLIE and E. N. JOHNSTON (*Biol. Bull.*, 1919, **36**, 225—273. Compare Lillie, A., 1918, i, 278).—If a piece of fine iron wire, wound round one end of a fine copper wire, is dropped into a 2% solution of egg-albumin containing 4% of potassium ferricyanide and 4% or more of sodium chloride, the entire surface of the iron wire rapidly becomes covered with fine, filamentous growths. They are characteristically regular in form; the majority are straight or slightly curved, and cease to grow at a length of 200 microns or less. A repetition of this experiment, using a 2% solution of egg-albumin containing 2% of potassium ferricyanide and 0.5% of sodium chloride, results in a slower growth, the form of the filaments is more irregular, and many larger structures are produced. In the stronger solution, growth usually ceases in about five minutes, whilst in the weaker solution it may continue for several hours. The action ceases when all the available potassium ferricyanide has been transformed, and may be renewed by adding more of the solution. The number of filaments may be limited by coating the metal with paraffin and removing the paraffin from very small areas before placing the metal in the solution. Experiments were made with iron, zinc, cobalt, cadmium, nickel, copper, lead, tin, chromium, and aluminium. For each metal which forms a precipitate with potassium ferricyanide there is a definite and characteristic type of precipitation structure. The presence or absence of a protective colloid has a marked influence on the kind of structure formed. Definite tubular filaments are produced from zinc, cadmium, and copper only in the presence of a protective colloid; in its absence, most of the precipitate appears "amorphous." Copper readily forms filaments in the absence of the protective colloid. The characters of structures produced with iron, zinc, cobalt, cadmium, copper, and nickel are described in detail. The form and rate of growth may be modified by the

passage of a weak electric current, by sudden changes in the concentration of the solution, and by the conditions of the surface of the metal, for example, whether rusty or not. All filaments are extremely sensitive to outside influences, such as jarring, causing currents, or addition of sand particles, any of which may cause change of direction of growth and change of form of filaments. Filaments grown on the surface show striking variations from those grown immersed. Certain metals, notably cadmium, show a rhythmic motion during growth. All these purely chemical and physical phenomena are significant in that they point the way to a better understanding of the phenomena of rhythm and periodicity in living beings.

CHEMICAL ABSTRACTS.

The Origin of Odour in the Molecules of Odoriferous Substances. HEINRICH TEUDT (*Prometheus*, 1919, 30, 201—204, 209—211; from *Chem. Zentr.*, 1919, iii, 138—139).—The author assumes that the origin of odour must be within the molecule, since the odour of a chemical compound is not, in general, affected by external influences as long as the molecule remains undecomposed. The source can scarcely lie within the atom, since, if this were so, every odoriferous atom must retain its odour in the free state and in combination with odourless atoms; the monatomic elements are, however, odourless, as are the ions of the strongly odoriferous halogens. The cause of the odour is to be sought between the atoms in the molecule which contain the valency electrons. It must be assumed that odours are caused by the vibrations of valency electrons, since the molecules of odoriferous substances are not altered in any way by the emission of odour. It appears probable that the nasal sensory nerves have electron vibrations which are increased by resonance when odoriferous particles having corresponding intramolecular electron vibrations are drawn into the nose in admixture with air. The author's investigations are explained by numerous diagrams. He is led to the conclusion that a chemical element can the more readily induce odour in its compounds in proportion as its electrons are more firmly united to the atomic nucleus. Metallic atoms, in consequence of the ease with which they detach electrons, are not suited to the production of odour. It can readily be seen that in all the horizontal series of the periodic system the power of giving odour increases as the metallic character of the element diminishes from left to right; correspondingly, the stability of the union between the atomic nucleus and the respective electrons increases from left to right. The author explains, further, the odourless or odoriferous character of certain substances, such as methane, ethane, the higher paraffins, carbon tetrachloride, etc., as well as the spread of odour to a distance and other phenomena.

H. W.

Place and Mode of Origin of the Acetone Substances. ERNST KERTESS (*Zeitsch. physiol. Chem.*, 1919, 106, 258—271).—Leucine was injected into the hind feet of dogs with an Eck's fistula and a "reverse" Eck's fistula. In the former case the injected sub-

stance is practically prevented from reaching the liver; in the second case, however, it does reach it. In the dogs with the "reverse" Eck's fistula, an increase in acetone, acetoacetic acid, and β -hydroxybutyric acid is recorded. The leucine does not alter the amount of excreted acetone substances in the dogs with Eck's fistula. The acetone substances, it is concluded, are therefore formed in the liver, and under certain physiological conditions they can be formed from leucine.

S. S. Z.

Chemical Studies in Physiology and Pathology. VIII. The Question as to Iodine Fixation in the Thyroid Gland.

E. HERZFELD and R. KLINGER (*Biochem. Zeitsch.*, 1919, **96**, 260—269. Compare A., 1918, i, 47, 241, 355, 357; this vol., i, 297).—The juices of pig's thyroid, human serum, and milk were treated with potassium iodide and $N/10$ -iodine, and then precipitated with hot 90% alcohol. A repeated extraction of the coagula with boiling water removed practically all the iodine which was retained. No iodine was removed in this way from untreated coagulated juice of thyroid. The amount of iodine extracted from the juice of thyroid by means of alcohol depended on the water content of the alcohol. The author considers that these experiments support the theory which he discusses, that iodine is a component part of the protein molecule of the thyroid gland, and that it is not an essential constituent of the thyroid secretion.

S. S. Z.

Alleged Irreciprocal Permeability of the Frog's Skin to Ions. MARTIN GILDEMEISTER and JUSSUF SCHÜKRI (*Biochem. Zeitsch.*, 1919, **96**, 241—248).—The authors cannot confirm the results obtained by Bayliss (A., 1908, ii, 712) that the skin of the frog conducts electric currents in Ringer's solution better from the outside to the inside than in the reverse direction. They therefore do not accept the conclusion arrived at by Bayliss that the skin of the frog is permeable to sodium ions from the outside, but not from the inside.

S. S. Z.

The Diazo-reaction of Normal Human Urine and the Influence of the Mode of Nutrition on the "Diazo Value."

OTTO FÜRTH (*Biochem. Zeitsch.*, 1919, **96**, 269—297).—The diazochromogen of normal human urine was investigated. Utilising his simplified method of isolating the hydroxyproteic acids from urine by decomposing the urea with soja urease, the author prepared a "baryta fraction" from the acid contents of the urine. The "baryta fraction" was further fractionated with various precipitating reagents before and after hydrolysis and the various fractions were studied. The conclusion arrived at is that diazochromogen, although not identical with histidine, is, however, a closely related iminazole derivative. Probably it consists of one or more transformation or condensation products of histidine produced by intermediate metabolism. Diazochromogen has further been found to be thermostable, soluble in alcohol, insoluble in ether, and separated only with difficulty by means of acetone from the alcoholic solution. It does not give Millon's reaction.

Another part of this investigation was devoted to the study of the "diaz value" and the "diaz quotient" of the urine of normal subjects, tubercular subjects in the early stage of the disease, underfed subjects who subsisted on a diet deficient in protein, and cachectic individuals. From these observations and those made by Masslow the author concludes that the iminazole complex contained in the diazochromogen is of endogenous origin. S. S. Z.

Oxidation Procedure in the Human Organism. WALTER LASCH (*Biochem. Zeitsch.*, 1919, **97**, 1—21).—As much as 12 grams per day of sodium thiosulphate can be consumed without harm. The thiosulphate is, however, not excreted as such in the urine, but is oxidised in the organism in accordance with the law observed by Tauber in the case of phenol. The ethereal sulphates increase slightly in the urine with intake of sodium thiosulphate. S. S. Z.

Origin and Significance of Acetoacetic Acid. L. C. MAILLARD (*Bull. Acad. med.*, 1919; from *J. Pharm. Chim.*, 1919, [vii], **20**, 185—187).—A considerable quantity of acetoacetic acid was formed in a solution containing *cycloglycylglycine*, glycerol, and yeast-cells. The author suggests that the production of acetoacetic acid in the human body is due to the reduction of the dipeptide (removal of amino-groups), and not to an oxidising process. This conception appears to be more in harmony with the restricted oxidising faculty of diabetic subjects. W. P. S.

Preparation and Physiological Action of some Derivatives of Meconic Acid. L. LAUTENSCHLÄGER (*Biochem. Zeitsch.*, 1919, **96**, 73—86).—The following derivatives of meconic acid were synthesised and tested for their physiological action. *Acetyl* derivative, $\text{OAc} \cdot \text{C}_5\text{HO}_2(\text{CO}_2\text{H})_2$, forms colourless needles, m. p. 218° . The *benzoyl* derivative crystallises in colourless leaves, m. p. 248° (decomp.). The *methyl hydrogen* ester forms colourless crystals, m. p. 161.5° ; the *dimethyl* ester has m. p. 117° ; the *propyl hydrogen*, *dipropyl*, and *diisobutyl* esters form colourless crystals, m. p. 165° , 105° , and 98° respectively; the *diamyl* ester is a colourless oil. The *urethane* derivative forms colourless crystals, m. p. 124° .

Meconylcarbamide, $\text{CO} \begin{array}{c} \diagup \text{C(OH):C} \diagdown \text{CO} \cdot \text{NH} \\ \diagdown \text{CH}=\text{C} \diagup \text{O} \\ \diagup \text{CO} \cdot \text{NH} \end{array} \text{CO}$, forms a yellow powder, m. p. 173° (decomp.), and its *ethyl*, *propyl*, and *allyl ethers* are white, crystalline powders, m. p. 138° , 141° , and 143° (all decomp.) respectively. *Meconylthiocarbamide* is a clear, yellow, crystalline powder, m. p. 181° (decomp.), and its *propyl ether* has m. p. 138° (decomp.).

The acetyl and benzoyl derivatives and the aliphatic ethers of the acid produce, like the original acid, slight paralysis in the frog, but are inactive in the rabbit. The ethyl, and to a greater extent the propyl, ester produces a more marked action in the frog than the original acid. The corresponding monoalkyl derivatives are also

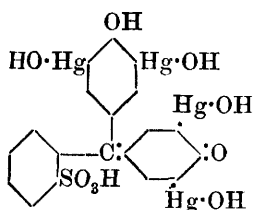
more active than the acid itself, but are not so potent as the normal esters. On the rabbit, however, this group of compounds produces no effect. The ether and diazo-compounds of the above esters behave physiologically like the esters themselves. The hydrazine derivative of meconic acid is very toxic and lethal in small doses.

The urethane derivative of meconic acid shows little potency, whilst the carbamide derivative is more active in the frog. The ethyl and propyl derivatives of the latter resemble meconic acid in their activity. Meconylthiocarbamide behaves like meconyl-carbamide, but is only one-third as potent. Its propyl derivative shows also some potency in the frog; in the rabbit the latter substances produce no effect. None of the synthesised substances has, therefore, manifested any definite narcotic action. S. S. Z.

Experimental Nephropathy produced by an Organo-mercury Compound of Phenolsulphonephthalein. J. EDWARD

BURNS, E. C. WHITE, and J. G. CHEETAM (*J. Urol.*, 1919, **3**, 1—16).

—As phenolsulphonephthalein and mercury have special affinities for the secreting cells of the kidney it was thought that a compound containing these substances would attack these cells and not attack the other organs of the body, and the changes thereby produced would more nearly resemble the different types of nephritis found in the human being than those produced with other substances. The compound synthesised was tetrahydroxymercuriphenolsulphone-



phthalein, which probably has the annexed formula. It contains 63% of organically bound mercury. It is soluble in dilute alkali hydroxide. When given to dogs this substance produced acute and chronic renal lesions which resemble quite closely those found in the different types of nephritis in human beings. The lesions of the acute type were mainly tubular, although some slight glomerular changes were noticed. In the chronic type the most characteristic change is the increase of interstitial tissue both in the glomeruli and between the tubules, together with areas of tubular obliteration and glomerular fibrosis. Chemical examination of the blood and urine following the intravenous injection of sodium chloride and urea after the method of Underhill, Wells, and Goldschmidt (*J. Expt. Med.*, 1913, **28**, 322), showed results quite analogous to the type of lesion produced. This organo-mercury compound produced no lesions elsewhere in the body.

CHEMICAL ABSTRACTS.

Chemistry of Vegetable Physiology and Agriculture

Comparative Studies on Respiration. VII. Respiration and Assimilation. W. J. V. OSTERHOUT (*J. Gen. Physiol.*, 1919, 2, 1—3).—Certain improvements in technique are described; thus when a reagent is employed which has a “buffer” effect it is desirable to have the same “buffer” action during the measurement of normal respiration as during exposure to the reagent. An indicator should be present in the liquid containing the organisms, so that changes in reaction may be observed. Preliminary results indicate that there is pronounced antagonism between such substances as sodium chloride and calcium chloride in their effect on respiration.

J. C. D.

Comparative Studies on Respiration. VIII. The Respiration of *Bacillus subtilis* in Relation to Antagonism. MATILDA MOLDENHAUER BROOKS (*J. Gen. Physiol.*, 1919, 2, 5—15).—In relatively low concentrations of sodium, potassium, and calcium chloride the rate of respiration of *B. subtilis* remains fairly constant for a period of several hours, whilst in higher concentrations there is a gradual decrease in the rate. The effects of salts on respiration show a well-marked antagonism between sodium chloride and calcium chloride and between potassium chloride and calcium chloride. The antagonism between sodium and potassium chlorides is slight.

J. C. D.

Comparative Studies on Respiration. IX. The Effects of Antagonistic Salts on the Respiration of *Aspergillus niger*. F. G. GUSTAFSON (*J. Gen. Physiol.*, 1919, 2, 17—24).—In relatively dilute solutions sodium chloride and calcium chloride increase the respiration of *Aspergillus* in the presence of dextrose. Higher concentrations cause a decrease, probably due to the osmotic effects of the salts. The antagonism between sodium chloride and calcium chloride could be demonstrated by a study of the respiration of this organism. Spores germinated on a medium containing 0.5*M*-sodium chloride and 0.05% of dextrose, but failed to do so when calcium chloride was used instead of sodium chloride, or when both salts were present. Apparently a substance may have different effects on respiration from those which it has on growth. J. C. D.

Proteinogenous Amines. IV. The Production of Histamine from Histidine by *Bacillus coli communis*. KARL K. KOESSLER and MILTON T. HANKE (*J. Biol. Chem.*, 1919, 39, 539—584).—*Bacillus coli communis* does not form histamine from histidine when acting alone, in the presence of nitrates or ammonium salts, or in a medium containing glycerol. When glycerol or dextrose and a source of nitrogen, such as potassium nitrate or ammonium chloride, are present, some 50% of the histidine is con-

verted into histamine. Under these conditions the medium becomes acid, and the suggestion is advanced that histamine is produced by the bacillus as a means of neutralising the acid produced from glycerol. Contrary to many statements, it is found that histamine is never produced except in the presence of an easily available source of carbon.

J. C. D.

Formation of d - β -Iminazoly-l-lactic Acid from l -Histidine by Bacteria. K. HIRAI (*Act. Schol. Med. Kyoto*, 1919, **3**, 49—53; from *Physiol. Abstr.*, 1919, **4**, 256).—Histidine hydrochloride, prepared from ox blood, was acted on for forty days in protein-free nutrient media with a strain of *Proteus vulgaris* which was capable of converting l -tyrosine into γ -hydroxyphenyl-lactic acid. The product was separated by precipitation with phosphotungstic acid; it crystallised with $1\text{H}_2\text{O}$ and had $[\alpha]_{\text{D}}^{19} + 33.7^\circ$, the yield being 11%. It was identified by elementary analysis and by means of the platinichloride.

H. W.

Application of the Fixation Method in Bacterial Fermentation. I. Acetaldehyde as an Intermediate Product in the Fermentation of Sugar, Mannitol, and Glycerol by *Bacillus coli*, Dysentery, and Gas Gangrene Organisms. C. NEUBERG and F. F. NORD (*Biochem. Zeitsch.*, 1919, **96**, 133—158).—By employing sodium sulphite and calcium sulphite as "fixing" agents, acetaldehyde has been established as an intermediate product in the fermentation of dextrose, mannitol, and glycerol. *B. coli* was employed in the fermentation of dextrose, Flexner Y and Shiga-Kruse cultures in the fermentation of mannitol and Fränkel's bacillus (*B. Welchii*) in the fermentation of glycerol. As the last-mentioned organism is an anærobe the possibility of the formation of acetaldehyde as a secondary product from the alcohol produced is excluded.

S. S. Z.

Application of the Fixation Method in Bacterial Fermentation. II. The Establishment of an Aldehyde Stage in Acetic Acid Fermentation. C. NEUBERG and F. F. NORD (*Biochem. Zeitsch.*, 1919, **96**, 158—175).—Alcohol was fermented in the presence of calcium sulphite with *Bacterium Orléanense*, *B. Ascendens*, and *B. Pasteurianum*. In each case acetaldehyde was established as an intermediate product in the fermentation.

S. S. Z.

Acid Fermentation of Xylose. E. B. FRED, W. H. PETERSON and AUDREY DAVENPORT (*J. Biol. Chem.*, 1919, **39**, 347—383).—Xylose is readily fermented by bacteria which are found in fresh silage, sauerkraut, and manure, and also in certain soils, but the organisms commonly studied in the laboratory failed to break down the sugar. The organisms which can effect the fermentation are readily isolated in pure culture. The fermentation takes place either in the presence of free oxygen or in a limited supply, and the main products formed are acetic acid and lactic acid. The

relation of acetic acid to lactic acid approaches the theoretical ratio of 40 to 60 that would obtain if these two compounds were the only products arising from fission of the xylose molecule. Traces of carbon dioxide and ethyl alcohol were detected. Other sugars are fermented by these xylose-fermenting bacteria. J. C. D.

Mode of Action of Metal Sols. C. R. MARSHALL (*Proc. Roy. Soc. Edin.*, 1918-19, **39**, 143-148).—An attempt to ascertain how silver in a particular form, such as colloidal silver solutions (Bredig), can exert a bactericidal action. The impact of the larger submicroscopic particle is not the cause, whilst there is no evidence that adsorption of the silver particle takes place on the surface of the organisms. Electropositive and electronegative sols produced the same antiseptic action. The concentration of free silver ions was insufficient to explain the pharmacological action, but when the size of the particles was considered it was found that the bactericidal value may be ascribed to the ultra-microscopic particle below $15\ \mu\mu$ in diameter. J. C. D.

Vitamine Requirements of certain Yeasts. FRED A. M. BACHMANN (*J. Biol. Chem.*, 1919, **39**, 235-257).—The observations of Pasteur and of Wildier on the nutritive requirements of yeast are confirmed. All the yeasts investigated grew better and fermented more readily in a medium containing some small amounts of organic material other than sugar. It is suggested that the substances which are necessary for fermentation to be carried out effectively by the yeast are of the nature of vitamins (Wildier's "bios," *La Cellule*, 1901, **18**, 313). The yeasts appear to vary considerably in their requirements for this accelerating factor. J. C. D.

Action of Radium Emanation on the Vitamines of Yeast. KANEMATSU SUGIURA and STANLEY R. BENEDICT (*J. Biol. Chem.*, 1919, **39**, 421-433).—This investigation showed that exposure to radium emanation may cause partial destruction of the vitamins present in yeast. It is suggested that a part of the beneficial influence of radium in the treatment of malignant tumours may be dependent upon such destruction of the growth-accelerating factors. J. C. D.

The Metabolin and Antibolin of Yeast. E. VAHLEN (*Zeitsch. physiol. Chem.*, 1919, **106**, 133-178).—The author has prepared metabolin and antibolin from yeast which, although not quite identical with the similar principles previously extracted by him from the pancreas of cattle, resembled them in their main properties. Metabolin accelerates alcoholic fermentation, antibolin has the opposite effect. The principles can be transformed into each other by molecular rearrangement. An irreversible metabolin has also been prepared from yeast and potatoes. This metabolin also accelerated alcoholic fermentation and reduced the amount of sugar in the urine of diabetic patients on two occasions. S. S. Z.

The Content and the Formation of Invertase in Yeast.

H. VON EULER and OLOF SVANBERG (*Zeitsch. physiol. Chem.*, 1919, **106**, 201—249).—The inversion capacity of two strains of yeast examined from time to time has been proved to be constant. The optimum temperature for invertase formation in one of these strains has been found to be 26—30°. When the temperature was raised by about 35° no invertase formation could be observed. The invertase formation is further dependent on the acidity of the medium. The maximum enzyme formation coincides with the optimum activity of the invertase. At a H-ion concentration higher than $P_H=2$ the invertase is destroyed; on the other hand, at a H-ion concentration of $P_H=6-7$ the enzyme formation is 90% of its optimum. Water at a temperature of 10° does not wash out the invertase of fresh living yeast. S. S. Z.

The Augmentation of the Catalase Activity of Yeasts.

HANS VON EULER and INGVAR LAURIN (*Zeitsch. physiol. Chem.*, 1919, **106**, 312—317).—The catalase of *Saccharomyces Thermantionum* is activated by chloroform, but not by an increase of temperature. Sunlight diminishes the action of catalase in living yeast cells, whilst X-rays have no effect on it. S. S. Z.

Ilex vomitoria as a Native Source of Caffeine.

FREDERICK B. POWER and VICTOR K. CHESNUT (*J. Amer. Chem. Soc.*, 1919, **41**, 1307—1312).—Since the so-called "Paraguay Tea," which contains considerable proportions of caffeine, is derived from certain South American species of *Ilex*, the authors have examined other representatives of this genus found in the south-eastern States in order to discover possible home sources of the drug. Several species were found to contain no caffeine at all, but *Ilex vomitoria*, Aiton, appears to be worth cultivating as a source of the base. Under the name "Yaupon," the leaves were already used by the Indians for their medicinal and stimulating properties. J. C. W.

Action of Cyanamide and of Dicyanodiamide on the Development of Maize.

P. MAZÉ, VILA, and M. LEMOIGNE (*Compt. rend.*, 1919, **169**, 804—807).—The results of water-culture experiments show that cyanamide at a concentration of 0.162 gram per litre prevents the germination of maize seeds, but that dicyanodiamide at this concentration is not toxic towards their germination.

Similarly, cyanamide, either with or without the presence of sodium nitrate, kills maize seedlings, whereas dicyanodiamide, in the presence of sodium nitrate, does not appreciably check the development of the plant, although with dicyanodiamide as the only source of nitrogen, the plant does not increase in weight, but yet remains alive for several months. W. G.

Presence of Formic Acid in the Stinging Hairs of the Nettle.

LEONARD DOBBIN (*Proc. Roy. Soc. Edin.*, 1918—19, **39**, 137—142).—Although it is frequently stated that formic acid is present in the stinging hairs of the nettle, few attempts at a direct

proof have been made. The author collected the acid present in a very large number of hairs by compressing the leaves with filter-paper impregnated with barium carbonate. From an examination of the barium salt formed he comes to the conclusion that free formic acid does exist in the stinging hairs. J. C. D.

The Yellow Colouring Substances of Ragweed Pollen.

FREDERICK W. HEYL (*J. Amer. Chem. Soc.*, 1919, **41**, 1285—1289).—The pigments of ragweed pollen may be extracted by alcohol, then precipitated in fractions from an aqueous solution by means of basic lead acetate, and finally recovered from the lead precipitates in the usual way, the yield being about 0.6%. The least soluble pigment is a quercitrin glucoside, $C_{21}H_{20}O_{12}$, which fuses at 228—229° to a cherry-red oil, and thus differs from its three known isomerides, quercimeritrin, isoquercitrin, and incarnatin. Among the more soluble glucosides is one which yields isorhamnetin on hydrolysis, and this seems to be predominant. J. C. W.

Soil-sorption. E. RAMANN and A. SPENGLER (*Landw. Versuchs-Stat.*, 1918, **92**, 127—146).—The interchange of bases occurring in mixed solutions containing two different bases has been studied by means of a permutite of moderately constant composition prepared in the wet way. The replacement of bases taking place when such a hydrated aluminium alkali silicate is treated with neutral potassium, ammonium, calcium, and sodium salts has the character of a chemical exchange, no signs of physical adsorption being detectable. The interchanges are by equivalents, that of potassium and ammonium following the law of mass action; the curves expressing the ratios of the ions in solution and those of the bases in the silicates are coincident. In solutions containing sodium and calcium salts the interchange of bases corresponds predominantly with the ratio of the ions in the solution, but preponderance of the calcium or sodium salts results in divergences dependent on a second factor of unknown nature. Potassium and ammonium are mutually replaceable, and displace sodium and calcium completely from the silicate; whereas the displacement of potassium and ammonium by sodium and calcium is incomplete. The ratios between the bases in the solutions and in the silicates have different values. Bases present in small proportions in the solutions are combined by the silicate in amounts greater than those corresponding with such proportions. Within wide limits, the absolute concentrations of the salts in the solution are without appreciable influence on the composition of the silicate, this being the case even with mixtures of calcium salts with those of the univalent metals. T. H. P.

Solubility of Calcium Carbonate of Different Origins and Degrees of Fineness in Water containing Carbon Dioxide in Relation to Soil and Plants. G. HAGER and J. KERN (*J. Landw.*, 1916, **64**, 325—342).—The degree of fineness of calcium carbonate influences considerably its solubility and especially its velocity of dissolution in water containing carbon dioxide.

The less prolonged the action and the greater the proportion of carbon dioxide in the water, the more marked are the differences observed with carbonates of different finenesses. The increased rapidity of dissolution, as well as the more effective distribution obtainable, probably causes the superior action on soil and plants of the more finely ground carbonate. T. H. P.

Determination of the Efficacy of the Soil Feeding Stuff, Phosphoric Acid and Potash, by Culture Experiments, and Determination of their Relative Solubility by Acids.

O. LEMMERMANN, A. EINECKE, and L. FRESenius (*Landw. Versuchs-Stat.*, 1916, **89**, 81—195).—A large number of pot experiments have been carried out with soils of different types, analyses of the soils especially as regards the relative solubilities of the phosphates and potassium compounds being also made. Determinations of such solubilities furnish in most cases a means of expressing the physiological efficiency of these fertilising substances. In the case of the phosphates, the best of the various solvents tried for determining the relative solubility proves to be 1% citric acid solution, and the soil may be extracted by dropping the solvent through it or by shaking it with the solvent. For potash, on the other hand, this solvent is too weak, and satisfactory results have been obtained by the use of 10% hydrochloric acid. In these determinations allowance must be made for the physical characters of the soil. The common assumption that the potassium compounds of the better soils are more difficultly soluble than those of the lighter ones is not supported by the results obtained; such assumption applies more in the case of the phosphates, this being perhaps attributable to the higher clay- and iron-contents of the better soils. The degree to which plants are able to utilise the phosphoric acid appears to increase with the poverty of the soil in phosphates. T. H. P.

Comparison of Two Fertilisers according to Mitscherlich's Law of the Minimum. MARYAN GORSKI (*Landw. Versuchs-Stat.*, 1919, **93**, 113—120).—Results obtained in fertilising experiments with increasing proportions of ammonium sulphate and sodium nitrate agree well with Mitscherlich's mathematical expression (A., 1911, ii, 760). It is shown that equality of the efficiency factors (*Wirkungsfaktoren*) for corn- and straw-yields necessitates constancy of the ratio, corn-yield:straw-yield, for different minimum factors. Calculation of the ratio between the efficiency factors for ammonium sulphate and sodium nitrate gives values which remain almost unchanged, no matter whether the efficiency factors of the corn-yield or those of the straw-yield are employed in the calculation. T. H. P.

JOURNAL

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THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN
BRITISH AND FOREIGN JOURNALS.

PART II.

General and Physical Chemistry.

Influence of Ultra-red Characteristic Frequencies on the Coefficient of Refractivity in the Visible Portions of the Spectrum. J. WIMMER (*Physikal. Zeitsch.*, 1918, 19, 483—486).

—A mathematical paper, in which it is shown that the relationship, which may be deduced from the Drude theory and the work of Dehlinger, may be used to calculate the influence of the ultra-red characteristic frequencies on the refractive index in the visible region. Further, the relationship gives a picture of the nature of the vibrations to which the characteristic frequencies are due. Corresponding with the k relationship for solids with two atoms or atomic groups in the molecule, a similar k relationship may be deduced by analogous methods for liquid substances with three atomic groups as origin of the ultra-red characteristic frequencies. In the case of monohydric alcohols, it is shown that in the ultra-red absorption spectrum the wave-lengths of the superposed harmonic absorption region are related as the roots of the masses of the vibrating atomic groups.

J. F. S.

Origin of Spectra. J. C. McLENNAN (*Proc. Physical Soc., London*, 1918, 31, 1—29).—The Guthrie lecture, in which the modern views of spectroscopy are discussed along with the methods of determination of spectra in the extreme ultra-violet. J. F. S.

Fundamental Frequencies in the Spectra of Various Elements. J. C. McLENNAN and H. J. C. IRETON (*Phil. Mag.*, 1918, [vi], 36, 461—471).—It is shown that when zinc and cad-

mium vapours respectively are bombarded by electrons the kinetic energy of which is gradually increased, monochromatic radiation is suddenly emitted by the vapour when the impact voltage is that given by the quantum relation for the frequency $\nu = (1.5, S) - (2p_2)$. When the impact voltage is increased beyond this amount, no additional radiation is observed until that corresponding with the frequency $\nu = (1.5, S) - (2, P)$ is applied. When these conditions are realised, the wave-lengths, the frequencies of which are given by $\nu = (1.5, S) - (2p_3)$ and $\nu = (1.5, S) - (2, P)$, are then recorded on the plates. It is also shown that when a bunsen flame is fed with the vapour of zinc, it is possible to obtain monochromatic radiation of wave-length $\lambda = 3075.99 \text{ \AA.U.}$ The evidence adduced, to show that the series of wave-lengths given by $\nu = (1.5, S) - (m, P)$, is probably fundamental from the point of view of electronic vibrations within the atoms of the elements mercury, zinc, cadmium, magnesium, calcium, and probably strontium and barium. J. F. S.

Ultra-violet Spectra of Magnesium and Selenium. J. C. McLENNAN and J. F. T. YOUNG (*Phil. Mag.*, 1918, [vi], **36**, 450—460).—The spectra of magnesium for (a) the spark in air, (b) the arc in air, and (c) the arc in a vacuum have been investigated in the region $\lambda = 2852.22 \text{ \AA.U.} - \lambda = 2000 \text{ \AA.U.}$, and some fifty-eight new lines have been observed. The existence of the line $\lambda = 2026 \text{ \AA.U.}$, first mentioned by Saunders, has been confirmed, and considerations are brought forward supporting the view that the series $\nu = (1.5, S) - (m, p_2)$ has a real existence. Twelve new lines are recorded in the selenium spark spectrum between $\lambda = 2200 \text{ \AA.U.}$ and $\lambda = 1850 \text{ \AA.U.}$ Five lines in the selenium arc have been found in the same region. In the sources used no part of the spectrum longer in wave-length than $\lambda = 2200 \text{ \AA.U.}$ was present. The adsorption spectrum of selenium metal in the carbon arc has been investigated and a reversal found at $\lambda = 1960 \text{ \AA.U.}$, which is the strongest line in both the spark and arc spectrum. If the absorption of selenium vapour should prove to be analogous to that of mercury, zinc, and cadmium, this would indicate that the two series $\nu = (1.5, S) - (m, P)$ and $\nu = (1.5, S) - (m, p_2)$ for selenium are in the extreme ultra-violet. J. F. S.

Measurement of the Short Wave-length Portion of the Cerium Arc Spectrum in Terms of the International Normal. PHILIPP KLEIN (*Zeitsch. wiss. Photochem.*, 1918, **18**, 45—83).—The short wave-length spectrum of cerium has been measured by means of a concave Rowland grating, 6.5 metres in diameter and ruled with 20,000 lines per inch. Cerium nitrate was vaporised in carbon, iron, and copper arcs for the purpose, and the spectra photographed. Long lists of the lines measured are given, and these are compared with the previous measurements of Exner and of Haschek and Bakowski. An accuracy of measurement of 0.003 Ångstrom unit is claimed over the range $2518.509 \mu\mu - 4546.066 \mu\mu$, this being the range investigated. The measurements were made

with the second order spectrum. The intensity of the lines is indicated, as also is the presence of doublets, reversed lines, and broadened lines. J. F. S.

The Arc Spectrum of Zirconium, Measured in Terms of the International Normal. W. VAHLE (*Zeitsch. wiss. Photochem.*, 1918, **18**, 84—137).—The arc spectrum of zirconium has been measured by means of a concave Rowland grating 6·34 metres in diameter and ruled with 787 lines per mm. Zirconium nitrate was vaporised in a carbon arc and the spectrum photographed. Long lists of the lines measured are given over the range 2285·229 $\mu\mu$ —7169·044 $\mu\mu$, and these are compared with the measurements of Bachem. An accuracy exceeding 0·005 $\mu\mu$ is claimed for the stronger lines. The measurements were made with the second order spectrum for wave-lengths below 5658 $\mu\mu$ and with the first order spectrum for larger wave-lengths. J. F. S.

Absorption Spectra of some Derivatives of cycloPropane. EMMA P. CARR and C. PAULINE BURT (*J. Amer. Chem. Soc.*, 1918, **40**, 1590—1600).—In order to investigate further the effect of ring-formation on absorption spectra, the authors have examined a number of cyclopropane derivatives, their ethylenic isomerides, and the corresponding open-chain compounds. The series includes (1) methyl γ -benzoyl- β -phenylethylmalonate, methyl 3-benzoyl-2-phenylcyclopropanedicarboxylate, and the two isomeric methyl β -benzoyl- γ -phenylvinylmalonates; (2) methyl anisoylphenylethylmalonate, methyl 3-anisoyl-2-phenylcyclopropanedicarboxylate, and the two isomeric methyl β -anisoyl- γ -phenylvinylmalonates; (3) methyl benzoylphenylpropylmalonate and the isomeric methyl benzoyl-2-phenyl-3-methylcyclopropanedicarboxylates; (4) $\alpha\gamma$ -dibenzoyl- β -phenylpropane, 1:3-dibenzoyl-2-phenylcyclopropane, and 1:3-dibenzoyl-2-phenylcyclopropene. (For preparation of these compounds, see Kohler and Conant, A., 1917, i, 566, 568.)

The authors find that the character of the absorption is closely related to the form of linking of the three central carbon atoms, and distinct differences in the absorption spectra of the corresponding cyclic, open-chain, saturated, and olefinic compounds are shown. In each series the cyclic substance shows an absorption quite similar to that of its open-chain analogue, but in every case the general absorption is greater. Evidently closure of the ring increases the absorptive power of the molecule.

Ring-formation in the cyclopropanes causes a shifting of the absorption towards the visible end, but to a less extent than in the case of the isomeric ethylenic compounds. These facts justify the conclusion that the cyclopropane ring is a centre of residual affinity similar in character, but intermediate in quantity to that of the double linking, and as such can form a conjugated system with a carbonyl group in the proper position.

The absorption spectra of four pairs of geometrical isomerides have been determined; in each pair the isomeride of lower m. p.

gave slightly greater general absorption and the isomeride of higher m. p. the greater tendency toward selective absorption. H. W.

Influence of Substituents of Reactions. III. Influence of Substituents on the Colour of Benzene Picrate. HARTWIG FRANZEN (*J. pr. Chem.*, 1918, [ii], **98**, 67—80).—The problem has been previously investigated in a series of experiments on the rate of reduction of substituted phenylhydrazines (A., 1918, i, 456); as data can only be slowly accumulated in this manner, the author has sought a more convenient method, and has examined the absorption spectra of a series of picrates of benzene and its derivatives. He is led to the following conclusions: A relationship exists between the influence of a substituent of the first order on the rate of reduction of phenylhydrazine and on the colour of benzene picrate; a substituent which increases the rate of reduction of the hydrazine deepens the colour of the picrate. The activity of the substituent depends on the degree of unsaturation of the atom united to the ring carbon atom; depth of colour increases with the degree of unsaturation. If the latter is decreased by introduction of another atom, the colour becomes brighter. Among the picrates of benzene derivatives with substituents of the first order, the meta-compounds are always the least and the para-compounds the most intensely coloured; ortho-compounds occupy an intermediate position, and are only slightly darker than the meta-compounds.

H. W.

Phenomena of Luminescence in Pyrazoline Derivatives. FRITZ STRAUS [with CARL MUFFAT and W. HEITZ] (*Ber.*, 1918, **51**, 1457—1477).—See this vol., i, 41.

Chemiluminescence. I. LIFSCHITZ (*Helv. Chim. Acta*, 1918, **1**, 472—474).—A preliminary account of work which is not yet completed.

Organomagnesium compounds of the type RMgX are very suitable for the study of chemiluminescence. Moeller (*Arch. Pharmaci Chemi*, 1914) has shown that the phenomenon only occurs with aromatic substances. It is now found that the difference between the aromatic and aliphatic compounds depends on the relative stability of the etherates; all ether-free Grignard reagents emit light in the presence of oxygen or nitrous oxide, but not of nitric oxide, nitrogen peroxide, carbon dioxide, and water. The additive compounds of organomagnesium substances with dimethylaniline are faintly luminescent in oxygen, but only in the case of aromatic derivatives.

The thermochemistry of the gradual addition of ether to suspensions of Grignard's reagents in benzene has been studied. With aliphatic reagents the greatest development of heat occurs when the first two molecules of ether are added, and very little heat is developed after the addition of four molecules; with aromatic reagents, on the other hand, the greater part of the heat is not

developed until four molecules of ether have been added, and further addition produces a still considerable effect. H. W.

Light Scattered by Gases ; its Polarisation and Intensity.

THE HON. R. J. STRUTT (*Proc. Roy. Soc.*, 1918, [A], **95**, 155—176).—The light scattered at right angles by gases and vapours is not completely polarised. The vibrations parallel to the existing beam have always an appreciable intensity, which in ordinary cases varies from 1·2% (pentane) to 14% (nitrous oxide) of the intensity in the perpendicular direction. Helium is an outstanding case, polarising far less completely than any other gas. The measurements give an intensity in the parallel component nearly half as great as that in the perpendicular component. Theory indicates that this is the ratio to be expected if vibration in the helium atom is limited to a direction fixed within the atom, on the assumption of random orientation to the exciting light. Such an atom is the antithesis of the spherical atom or molecule which would give perfect polarisation. The intensity of scattering by the different gases tried varies as the square of the refractivity, within the limits of experimental error. Saturated vapours, even when very dense, show no increase of scattering power beyond what is expected from the density. If molecular aggregates are formed they are not numerous enough to show by this method. Liquid ether apparently scatters about seven times less light than a corresponding mass of ether vapour.

J. F. S.

Rotation Dispersion and Inversion of *l*-Menthone.

HERMANN GROSSMANN and KURT BRAUER (*J. pr. Chem.*, 1918, [ii], **98**, 9—66).—The rotation dispersion of *l*-menthone has been determined for a large number of solvents at 20°; the specific rotation (for $c=5$) varied from -13° to -25° , and from -35° to -60° in red and violet light respectively. The dispersion-coefficient, $[\alpha]_v/[\alpha]_r$, lay between 2·16 and 2·80. Certain *d*-menthones have been obtained by inversion of *l*-menthone by concentrated sulphuric acid, according to Beckmann's method; determination of their dispersion-coefficients proves that they are not optical antipodes of *l*-menthone.

The rotation dispersion of *l*-menthone after being boiled with organic acids has been investigated in the actual solutions, which were found to be dextrorotatory, and the observations have been confirmed by examining the rotation dispersions of the menthones separated from such solutions either by water or by distillation. The values of $[\alpha]_v/[\alpha]_r$ lay between 3·12 and 3·67 for the solution and between 3·25 and 3·68 for the separated menthone. *l*-Menthone remains lævorotatory after being boiled with acetic anhydride; the dispersion-coefficient of the dissolved and separated menthone is abnormally low (1·73 and 2·01 respectively).

l-Menthone exhibits mutarotation when dissolved in formic acid or bromoform; the inversion in concentrated sulphuric acid solution

has been polarimetrically examined, and mutarotation has been observed.

The rotation-dispersion of *l*-menthone in alcoholic potassium hydroxide and hydrochloric acid solution has been investigated; the rotation is immediately positive, and is unchanged by heating. The value $[\alpha]_D/[\alpha]_T$ is unusually high, amounting to 4.35 or 3.87 for solutions and 5.07 or 5.57 for the separated menthones. When *d*-menthone is dissolved in alcoholic potassium hydroxide, the rotation falls noticeably, thus differing from its behaviour in formic and sulphuric acids, in which the rotation remains constant.

The gradual inversion of *l*-menthone at its boiling point has been investigated by a study of the rotation dispersion. An instance of abnormal rotation dispersion is here encountered, and the occurrence of a definite end-point, which is not altered by protracted heating, is established. The same end-point is reached more rapidly if *d*-menthone is used as initial material. The dispersion-coefficients at first decrease, then increase, and become infinitely great at zero, and subsequently sink until the value 3.47 is obtained; this value is exhibited by the so-called *d*-menthone.

The optical behaviour of *d*-menthones has been examined in a number of solvents; the specific rotation is found to be invariably increased in solution, whilst that of *l*-menthone is depressed. The dispersion-coefficients varied from 3.13 to 3.26.

The intra-molecular transformation suffered by *l*-menthone when heated appears to depend on desmotropy, equilibrium between the ketonic and enolic forms being slowly attained.

Inversion of *l*-menthone by various solvents is attributed to the additive or substitutive action of the latter, and the formation of *d*-menthone is due to a type of Walden inversion, this substance being formed by decomposition of intermediate products which are probably only stable in solution.

The influence of solvents on the specific rotation of optically active substances is due to reactions occurring between solvent and solute, for which the alteration in rotation is a particularly sensitive indicator.

H. W.

Law of Blackening of Layers Sensitive to Light. F. HALLA and A. SCHULLER (*Zeitsch. physikal. Chem.*, 1918, **93**, 173—182).—In a previous paper (*Zeitsch. wiss. Photochem.*, 1912, **11**) a relationship was put forward between the depth to which a film sensitive to light is darkened by light and the time of exposure. The relationships are now exactly and mathematically formulated. The calculations are extended to the case where the film lies on a reflecting base. The scattering of light is insufficient to explain the peculiarities observed in the blackening curves. The reflection of the base is shown to change, not only the depth of the blackening, but also the definition of the picture.

J. F. S.

The Radioactive Properties of the Mineral Springs of Colorado. O. C. LESTER (*Amer. J. Sci.*, 1918, [iv], **46**, 621—637).—The emanation content of more than 100 spring waters from Colorado

has been measured, and also the radioactivity of numerous samples of spring deposits. A high average activity of the waters was found, the most active examined showing the highest activity of any in the United States and surpassed only by a few foreign springs. For five springs the emanation content exceeded 100 (curies $\times 10^{-10}$ per litre), the highest being 305, and ninety-five springs exceeded 10. Of the latter, 75% were in or near metamorphic and igneous formations, but some of the most active were in sedimentaries. Thorium emanation was detected in only one spring. No springs of extraordinarily high emanation content were found, and although radioactive ores are abundant there are no large springs found near them. The measurements were for the most part carried out in the field by boiling out the water by Boltwood's method. F. S.

Thorium-Lead. KASIMIR FAJANS, F. RICHTER, and (FRL.) J. RAUCHENBERGER (*Sitzungsber. Heidelberger Akad. Wiss.*, 1918, pp. 28; from *Chem. Zentr.*, 1918, ii, 438—439).—According to theory, in addition to ordinary lead, there must be at least two members of the lead series with different atomic weights; on the one hand, radium-*G* or radium-lead, the final product of the uranium-radium series with an atomic weight 205·94, and, on the other, thorium-lead (Th-*D*), the atomic weight of which is calculated from that of thorium to be 208·08. Radium-*G* would be expected to occur in uranium minerals free from thorium, whilst thorium-lead must be looked for in thorium minerals free from uranium. The problem of isolating the latter is rendered difficult by the fact that thorium minerals free from uranium do not exist, whilst those poor in uranium are scarce. A mineral is unsuitable for investigation if it does not contain at least 4—5 times as much thorium as uranium, provided that thorium-lead and uranium-lead are either completely stable elements or have an approximately equal life period. The lead content of certain thorium minerals appears to point to the conclusion, however, that thorium-lead is relatively unstable, thus adding to the difficulty of its isolation.

The authors have examined a sample of thorite containing 30·10% of thorium, 0·44—0·45% of uranium, 0·35% of lead, in addition to unestimated amounts of silica, iron, rare earths, and traces of bismuth. The mineral was treated with fuming hydrochloric acid in glass flasks, in which decomposition is effected far more rapidly than in porcelain dishes. The solution was evaporated to dryness and the silica removed. Before precipitation of lead with hydrogen sulphide, the ferric iron was reduced to the ferrous state by means of hydroxylamine, and subsequent operations were conducted in an inert atmosphere. The lead was precipitated as sulphide, and converted first into the chloride and then into the sulphate, of which 4 grams were obtained. The mean of three analyses (performed by Höngschmid) gave as atomic weight $207·90 \pm 0·013$. On the supposition that uranium-lead and thorium-lead are perfectly stable elements, the whole of the lead separated from the thorite taken should have an atomic weight lying between the limits 207·97 and

208.00 if the atomic weight of thorium is taken as 232.12, that of helium as 4.00, and that of thorium-lead as 208.08. When the slight experimental and theoretical uncertainties are taken into consideration, the agreement between the practical (207.90) and theoretical (208.00) values may be regarded as satisfactory, and there is therefore no good reason for supposing that thorium-lead is not a stable element. If the slight discrepancy is actual, it is probably to be explained by the presence of ordinary lead (atomic weight 207.2); if, however, it is to be ascribed to the instability of thorium-lead, the lower limit for the half period of the element regarded as a uniform material is calculated to be 1.7×10^8 years. In any case, the existence of thorium-lead, obtainable in weighable amount and with an atomic weight approximating to 208.0, is placed beyond doubt. H. W.

Electrochemical Behaviour of Metals. A. SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **21**, 158—171).—A theoretical paper, in which the relationships and equilibria between metal atoms, ions, and electrons are considered in the case of attackable metals (zinc) and non-attackable metals (nickel). These relationships are considered with regard to the potential difference between the metals and solutions of their ions and to the action of acids on the metals. In the first place, the consideration deals with equilibrium and velocity of the changes, both being considered in connexion with the Nernst solution theory, and in the second place the relationships are dealt with on the basis of the phase rule, Δx diagrams being evolved for the case of zinc and nickel as representing attackable and non-attackable electrodes. J. F. S.

Passivity of Chromium. III. A. H. W. ATEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **21**, 138—150. Compare A., 1918, ii, 183, 193).—A theoretical paper, in which the reasons for the activation of passive chromium by cathodic polarisation are discussed. J. F. S.

Activation of Carbon Monoxide by Metallic Copper, the Generator Gas-cell and the Electromotive Activation of Alkali Formates. K. A. HOFMANN (*Ber.*, 1918, **51**, 1526—1537).—The author's discovery (this vol., ii, 23) that carbon monoxide in the presence of oxygen is rapidly oxidised to carbon dioxide at the ordinary temperature at a copper surface moistened with an alkali hydroxide has enabled him to realise the generator gas-cell, $O|Cu|alkali|Cu|CO$, and the drawbacks common to most of such cells have been overcome (subject of a censored patent). The *E.M.F.* ($CO \rightarrow CO_2$) is found to be 1.32 volts at 20°, which compares well with the value 1.343 volts at 17°, calculated by Nernst and von Wartenberg from the dissociation of carbon dioxide. The present paper deals with the purely scientific aspect of the problem. It is shown that the activation of the carbon monoxide is not due to the formation of an alkali formate. The suggestion is made that

a labile isoformate, $\text{OH}\cdot\text{C}\cdot\text{OK}$, is produced; its formation is only minimal at the ordinary temperature when carbon monoxide and an alkali alone are present, but is stimulated in the presence of copper. C. S.

Dissociation of Strong Electrolytes. NIELS BJERRUM (*Zeitsch. Elektrochem.*, 1918, **24**, 321—328).—A theoretical paper, wherein an hypothesis is developed according to which the strong electrolytes are completely dissociated. Because of the electrical forces between the ions, these electrolytes exhibit decreasing osmotic pressure, conductivity, and activity with increasing ion concentration. These decreases can be expressed by means of three numerical coefficients. A thermodynamic relationship between the activity and osmotic coefficients is developed and an approximate formula for the activity coefficient is worked out. The activity-coefficient possesses considerable chemical interest, and methods are outlined by means of which it may be determined, and in this connexion it is shown that the so-called neutral salt action, the anomalies of strong electrolytes, and the catalytic action of undissociated molecules only occur because the conductivity-coefficient has been used in calculations where more accurately the activity-coefficient should have been employed. J. F. S.

Ionic Migration in Liquid Crystals of Hydrated Ammonium Oleate. O. LEHMANN (*Ann. Physik.*, 1918, [iv], **57**, 244—256).—The changes effected in the appearance of liquid crystals of hydrated ammonium oleate under potential differences of 0—100 volts have been studied microscopically and with the aid of crossed nicols. The liquid crystal was contained in a capillary of 0.06 cm. diameter, and contact made with two platinum electrodes by means of a drop of ammonia solution saturated with ammonium chloride. The appearance at the electrodes, using various potentials, is described, and it is shown that the main cause of the observed phenomena is the re-formation of the hydrate of ammonium oleate from the ions which have migrated from the tube, and the taking up of these by the molecules present. J. F. S.

Mechanism of Cathodic Metal Separation. V. KOHLSCHÜTTER and E. VUILLEUMIER (*Zeitsch. Elektrochem.*, 1918, **24**, 300—321).—The electrolytic deposition of nickel from various solutions and under a series of different conditions has been studied with the object of finding an experimental connexion between the chemical polarisation and the form of electrolytically deposited metals. To ascertain this, the characteristic internal tension, which electrolytic nickel possesses, was investigated by depositing the metal on a platinum sheet and following the bending of the sheet. By this means it is shown that from the first moment the deposit undergoes a contraction which increases with further deposition. Consequently two processes must occur successively: first the formation of a film on the cathode, followed by a contraction of the film.

When the nickel is dissolved from such a contracted cathode the metal of the cathode returns to its original form. Consequently, the amount of bending corresponds with an equilibrium position, and the observation of the bending with time under stated conditions leads to characteristic curves. The process is dependent on the current density, and the composition of the electrolyte. It is strongly influenced by the addition of other substances to the electrolyte, and is less in solutions which cause an evolution of hydrogen, and also when the deposit is fine grained. When an already bent cathode is charged with hydrogen it straightens out again, but if the current is interrupted at this stage, the hydrogen is set free and the cathode takes up its original bent form. In solutions which do not evolve hydrogen the contraction occurs in jumps, which have the characteristics of delayed effects. The whole effect probably is due to the fact that the metal is at first deposited in a highly disperse form, and then the particles sinter with the formation of a denser material. This probably occurs along with the formation of a gas layer on the cathode, which plays the part of a dispersion medium. Since the electrolytic solution pressure of the highly disperse form is necessarily greater than that of the denser metal, this view explains the increase in the deposition potential above that of the ordinary metal.

J. F. S.

The "Curie Point" of Pure Iron and Ferrosilicon.

A. SANFOURCHE (*Compt. rend.*, 1918, **167**, 683—865).—It was shown by Curie that at about 1280° the magnetic property of iron was suddenly increased, in the ratio of about 3 to 2, and he termed this state of iron between 1280° and its melting point, δ . Pure iron prepared by the author melted at 1515°, and when slowly cooled its magnetic property suddenly changed at 1310°, whilst, on re-heating the iron, the break in the curve occurred at 1365°. This critical point is the "Curie point," A_4 . The temperature at which it is shown is rapidly, though slightly, lowered by the addition of silicon in amounts up to 1% (1281°); above that amount the magnetic change is smaller, and with amounts of silicon in excess of 2.5% (1195°) is no longer perceptible.

C. A. M.

A Relation between Boiling Points at One Atmosphere and in a "Vacuum."

W. P. JORISSEN (*Zeitsch. anorg. Chem.*, 1918, **104**, 157—162).—Since the critical temperature of any substance is approximately equal to twice the boiling temperature (absolute) in a vacuum (20 mm.) and to 1.55 times the boiling temperature at atmospheric pressure, it follows that the ratio of the two boiling temperatures, $T_{(20 \text{ mm.})}/T_{(1 \text{ atm.})}$ is a constant, equal to 0.78. This ratio is shown to be constant for a large number of substances, both organic and inorganic. The constancy of the ratio can be deduced from van der Waals's vapour pressure formula and from the results of a number of independent workers.

E. H. R.

Latent Heat of Fusion as the Energy of Molecular Rotation.

KÔTARÔ HONDA (*Sci. Rep. Tohoku. Imp. Univ.*, 1918, **7**, 123—130).—A theoretical paper, in which the author develops the equation $w\lambda/T_m = nE_{T_m}/2T_m$, in which T_m is the melting point in absolute degrees, E is the molecular energy belonging to each degree of freedom of the molecules, and $n=2$ or 3. This equation is tested by evaluating both sides and comparing the results for a number of elements. The equation is based on the assumption that during melting very little energy is required for internal or external work, and the numerical results show that for elements of group I this assumption is fully justified. In the case of a second group of elements which includes bismuth, tin, iodine, gallium, bromine, and chlorine, the values of $w\lambda/T_m$ are much greater than those for $nE_{T_m}/2T_m$. In the case of compounds, agreement between the two sides of the equation can be obtained if n is taken as larger than 2, that is, if the molecules have more than two degrees of freedom for rotation. This implies that compounds have a molecular structure both in the liquid and solid states. J. F. S.

The Course of the Values of a and b for Hydrogen at Different Temperatures and Volumes. III. and IV. J. J. VAN LAAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **21**, 1—15, 16—25. Compare A., 1918, ii, 185, 291).—Theoretical papers, III. continuing the discussion of the pressure-volume relations in relation to the variability of a and b , whilst in IV. the value of a below the limiting temperature is discussed. A series of mathematical addenda to the previous papers are added. J. F. S.

Relationships between Absolute Temperatures and the Corresponding Absolute Pressures of Moist Vapours. O. VENATOR (*Zeitsch. physikal. Chem.*, 1918, **93**, 242—244).—A short, critical discussion of the van der Waals's equation and its corollaries. It is shown that the value of a is a variable one, having minima at the absolute zero and at the critical temperature, and increasing to a maximum as the temperature is raised or lowered respectively. J. F. S.

Raoul Pictet's Equation of Condition for Moist Vapours. O. VENATOR (*Zeitsch. physikal. Chem.*, 1918, **93**, 245—246. See preceding abstract).—A criticism of Pictet's equation of condition for moist vapours. It is shown that this equation may be expressed in the form of the van der Waals's equation, and further that neither of these equations supplies the needs of the physico-chemical technology. J. F. S.

Relationship between Absolute Temperature and Absolute Pressure in Kilograms per Square Cm. for Moist Vapours. O. VENATOR (*Zeitsch. physikal. Chem.*, 1918, **93**, 247—249. See preceding abstracts).—The author deduces from the van der Waals's

equation the expression $\alpha = (T_k / T - 1) / (\log p_k - \log p)$, in which T_k is the absolute critical temperature, p_k the corresponding pressure in kg./sq. cm., T any temperature between T_k and the absolute zero, p the pressure corresponding with T . J. F. S.

Negative Adsorption. L. BERZELLER (*Biochem. Zeitsch.*, 1918, **90**, 290—293).—Negative adsorption was observed in experiments with starch as adsorbent with both lactose and maltose. With coagulated albumin, negative adsorption was observed with dextrose, lactose, maltose, and sucrose. S. B. S.

Dissociation of Salicylic Acid. R. ORTHNER (*Zeitsch. physikal. Chem.*, 1918, **93**, 220—235).—Salicylic acid, when heated at 200° under pressures of from 10 cm. to 120 cm. of mercury is dissociated into phenol and carbon dioxide to the extent of 98—82%. The decrease in dissociation with pressure is shown to be in accord with the law of mass action. J. F. S.

Reversal of the Dissociation of Salicylic Acid. R. ORTHNER (*Zeitsch. physikal. Chem.*, 1918, **93**, 236—239. See preceding abstract).—The dissociation of salicylic acid at 200° has been measured at various pressures of phenol and carbon dioxide. It is shown that just as the dissociation of salicylic acid follows the law of mass action, so the reversal of the dissociation by these substances is strictly in keeping with the requirements of the mass action law. J. F. S.

[**Dissociation of Salicylic Acid.**] EMIL BAUR (*Zeitsch. physikal. Chem.*, 1918, **93**, 240—241. See preceding abstracts).—A theoretical explanation of some of the points arising out of the previous papers. J. F. S.

Thickness of the Capillary Layer of Carbonic Acid. G. BAKKER (*Zeitsch. physikal. Chem.*, 1918, **93**, 154—172).—A theoretical paper, in which methods of calculating the thickness of the capillary layer are deduced. These methods are then applied to the case of carbon dioxide. Making use of formulæ previously published (A., 1916, ii, 553), the equation $\epsilon = -A/(v + \beta) + f(t)$ is deduced for calculating the energy of the homogeneous phases. In this equation A represents an arbitrary temperature function. The equation is arrived at by neglecting a small factor of a general equation, and a correction to compensate for this is applied to the resulting energy value. From the same original formula the value of ζ , the thickness of the capillary layer, is calculated from the equation $-4T^2[d(H/\zeta T)/dt] = (\rho_1 - \rho_2)r_i + 2\{\epsilon_3 - (\epsilon_1 + \epsilon_2)/2\}(\rho_1 + \rho_2)^2$; this equation may be integrated and the integration constant evaluated, since $H/\zeta T = 0$ at the critical temperature. A third method of calculating the thickness of the capillary layer is afforded by means of the equation $\zeta = H/(p_N - p_T)$ where p_N is the vapour pressure and p_T the pressure in the long direction of the capillary layer.

As mean values for carbon dioxide, by all three methods, the following are obtained for ζ :

t	-30° .	-10° .	0° .	10° .	20° .	25° .	30° .
ζ	1.46	1.72	1.91	2.21	3.51	7.06	26.1 $\mu\mu$

The differences between the values calculated by the different methods do not constitute an objection to the present theory, but are due to the differences of the equation of condition used.

J. F. S.

The Diffusion of Electrolytes into Jellies. I. The Relationship between the Distance of Diffusion and the Concentration. OTTO VON FÜRTH and FRANZ BUBANOVIC (*Biochem. Zeitsch.*, 1918, **90**, 265—287).—Chlorides were allowed to diffuse into gelatin jellies containing silver nitrate, and the rate of diffusion could thus be measured by the silver chloride precipitate. If d = the distance of diffusion and k = concentration, it was found that after a time t , $d = mt^{\frac{1}{2}}k^n$, where m and n are constants. The constants vary with the properties of the jellies. n has the same value for the same jelly when different electrolytes are used. It has been found to vary between 0.10 and 0.31.

S. B. S.

Dialysers made from Colloidal Membranes. L. BERCELLER (*Biochem. Zeitsch.*, 1918, **90**, 302—304).—Some remarks on the adsorption of iodine by collodion membranes, and the alteration of the permeability of the membranes according to whether they are treated with water when the organic solvent is still in them or they are nearly freed therefrom.

S. B. S.

Colloid Chemistry and its Industrial Application. F. G. DONNAN, W. C. MCC. LEWIS, E. F. ARMSTRONG, and A. S. SHORTER (*Rep. Brit. Assoc.*, 1917, 20—105).—The first report of the committee appointed to compile information regarding the advances made in capillary and colloid chemistry with special reference to industrial processes. The various branches of the subject have been dealt with by specialists, and the following are included in the report: (1) viscosity of colloids, 3 pp., Emil Hatschek; (2) colloid chemistry of tanning, 15 pp., H. R. Procter; (3) general review and bibliography of dyeing, 19 pp., P. E. King; (4) colloid chemistry in the fermentation industries, 3 pp., Adrian J. Brown; (5) caoutchouc, 5 pp., Henry P. Stevens; (6) colloid chemistry of starch, gums, hemicelluloses, albumin, casein, gluten, and gelatin, 32 pp., H. B. Stocks; (7) colloids in the setting and hardening of cements, 4 pp., C. H. Desch; (8) nitrocellulose explosives from the point of view of colloidal chemistry, 2 pp., E. R. Chrystall; (9) celluloid from the standpoint of colloidal chemistry, 2 pp., E. R. Chrystall. Very full bibliographies are included in each of the sections.

J. F. S.

Influence of Filtration on Hydrosols. TADEUSZ MALARSKI (*Kolloid Zeitsch.*, 1918, **23**, 113—122).—The effect of filtration on

hydrosols of ferric hydroxide and silver, both alone and in the presence of electrolytes, has been determined by measuring the rate of motion towards the electrodes in an electric field. The experiments show that filtration, through filter-paper, fat-free cotton, glass wool, and sand has a very marked effect on the rate of motion of positive hydrosols and also on negative hydrosols the charge of which has been reduced or changed by the addition of electrolytes. This phenomenon is explainable by the theory of contact electrification. By successive filtration of ferric hydroxide sol through filter-paper, the potential difference of the double layer is diminished, and consequently the velocity in an electric field is also diminished; repeated filtration will reduce the potential difference to zero and finally change the sign of the charge. Solutions of silver which have been treated with aluminium sulphate so that macroscopic particles are visible on filtration become stable for weeks. This is to be explained by the retention of the aluminium ion by the filter-paper.

J. F. S.

Spontaneous Transformation to a Colloid State of Solutions of Odorous Substances by Exposure to Ultra-violet Light. H. ZWAARDEMAKER and F. HOGEWIND (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **21**, 131—137).—A number of solutions of odorous substances in water, glycerol, or paraffin are found after keeping for several weeks to have passed into the colloidal condition. The action is much more rapid in daylight than in the dark, whilst in the presence of ultra-violet light the action is still more rapid; in the case of many substances the transformation only occurs in the presence of ultra-violet light. The colloid particles are shown to be negatively charged. Among the substances examined, the following in decreasing order show a marked Tyndall cone: (1) in water solution: eugenol, cresol, guaiacol, carvacrol, citral, cumidine, thymol, and hyponone; (2) in glycerol solution: eugenol, safrole, cresol, nitrobenzene, and apiole; (3) in paraffin solution: aniline, eugenol, and cumidine.

J. F. S.

Amphoteric Colloids. I. Chemical Influence of Hydrogen-ion Concentration. J. LOEB (*J. Gen. Physiol.*, 1918, **1**, 39—60; from *Physiol. Abstr.*, 1918, **3**, 406).—At its isoelectric point, gelatin is undissociated. In acid solution, it forms cations only; in alkaline solutions, anions only. On the acid side of the isoelectric point, amphoteric colloids can combine only with anions of neutral salts; on the alkaline side, only with cations. At the isoelectric point, an amphoteric colloid cannot combine with either the cation or the anion of a neutral salt.

H. W. B.

Inversion of Sucrose by Colloidal Silicic Acid. ALBERT MARY and ALEXANDRE MARY (*Compt. rend.*, 1918, **167**, 644—646).—Colloidal silicic acid, prepared by the action of hydro-

chloric acid on sodium silicate solutions and subsequent dialysis, hydrolyses sucrose fairly rapidly. The activity of the dialysed solutions begins to diminish after a period depending on the concentration of the colloid; 8% solutions retain their full activity for five to six hours, and 1.5% solutions for several months. Feeble hydrolysing power is exhibited also by solutions which have not been dialysed, but rendered faintly alkaline with sodium hydrogen carbonate solution; for these solutions there is an optimal temperature below 100° , varying according to the conditions, such as concentration of electrolytes. Coagulation of such solutions, whether spontaneous or accelerated by heating, is associated with loss of hydrolytic activity. If non-dialysed solutions are rendered faintly alkaline with sodium silicate solution instead of sodium hydrogen carbonate, they show a higher inverting power, and heating neither produces coagulation nor destroys their activity.

The conclusion is drawn that hydrolytic activity is a function of the degree of dispersion of the colloid, and that rise in temperature increases the activity (as in the case of acid hydrolysis) but eventually produces changes in the degree of dispersion, culminating in coagulation, which set a limit to the increase. The optimal temperature observed in inversion by colloidal metals and by invertase is probably to be accounted for on similar lines.

J. H. L.

Equilibrium between Carbon Monoxide, Carbon Dioxide, Sulphur Dioxide, and Free Sulphur. J. B. FERGUSSON (*J. Amer. Chem. Soc.*, 1918, **40**, 1626—1644, 1900).—The reaction $\text{CO} + \frac{1}{2}\text{SO}_2 \rightleftharpoons \text{CO}_2 + \frac{1}{4}\text{S}_2$ has been studied, and the equilibrium constants at 1000° and 1200° have been determined. The experiments were made by the "stream" and "semi-stream" methods both with and without contact substances. As contact substances, broken porcelain and platinised porcelain were used. It is shown that in all probability small quantities of carbonyl sulphide are also formed. The experimental data have been used to calculate the thermodynamic constants of the reaction and the free energy equations of this reaction, and also of the formation of sulphur dioxide from its elements.

J. F. S.

Influence of Substitution in the Components of Binary Solutions Equilibria. XII. Binary Solutions Equilibria between Acid Amides and Phenols and their Derivatives.

ROBERT KREMANN and ALOIS AUER (*Monatsh.*, 1918, **39**, 441—493).—Fusion and solidification curves have been prepared for the following binary mixtures: (1) acetamide with the three nitrophenols, (2) benzamide with the three nitrophenols, (3) acetamide and salicylic acid, (4) benzamide and the three hydroxybenzoic acids, (5) acetamide and the three dihydroxybenzenes, and (6) benzamide with the three dihydroxybenzenes. Acetamide and *o*-nitrophenol form no compounds, but a simple eutectic at 41.2° with ca. 5% of acetamide. Acetamide forms compounds with equi-

molecular quantities of both *m*- and *p*-nitrophenol, which melt at 51.5° and 96.1° respectively. Benzamide and *o*-nitrophenol form no compounds, but a simple eutectic, m. p. 41.8°, with 5% benzamide. Benzamide and *p*-nitrophenol form an equimolecular compound, m. p. 97.2°. Acetamide and salicylic acid form a compound in the proportion of two molecules of the former to one of the latter, m. p. 108°, and a further compound in equimolecular quantities, m. p. 116°. Benzamide and *p*-hydroxybenzoic acid form a compound in equimolecular proportions, and also one with three molecules of benzamide to one molecule of *p*-hydroxybenzoic acid. Acetamide and quinol form an equimolecular compound, m. p. 101°; resorcinol and acetamide form a compound with two molecules of the latter to one of the former compound, m. p. 37.5°. Benzamide and quinol form a compound of two molecules of the former to one of the latter, m. p. 103.8; an equimolecular compound, m. p. 88.1°, is formed between resorcinol and benzamide.

J. F. S.

Formation and Decomposition of Phloroglucinolcarboxylic Acid. G. PIAZZA (*Zeitsch. physikal. Chem.*, 1918, **93**, 183—219).—The equilibrium constant of the decomposition of the potassium salt of phloroglucinolcarboxylic acid, according to the equation $C_6H_2(OH)_3 \cdot CO_2K + H_2O \rightleftharpoons KHCO_3 + C_6H_3(OH)_3$, has been determined by titration with standard acid, using fluorescein as indicator, and taking as the end of the titration that point at which the fluorescence just disappeared. The velocity of formation and decomposition of potassium phloroglucinolcarboxylic acid has been determined at 50°. The course of the reaction was followed by the refraction of a beam of light, and was observed by means of a Lowe's interferometer. The velocity of decomposition was also followed by titration and by electrical conductivity measurements. Contrary to the usually observed behaviour, it is shown that the formation occurs much more slowly than the decomposition.

J. F. S.

The Inflammation of Mixtures of Methane and Air in a Closed Vessel. RICHARD VERNON WHEELER (*T.*, 1918, **113**, 840—859).

Hydrolysis of Ethyl Acetate by Alcoholic Sodium Hydroxide. RUD. WEGSCHEIDER and (FRL.) LILLY RIPPER (*Monatsh.*, 1918, **39**, 325—373).—The hydrolysis of ethyl acetate by solutions of sodium hydroxide in alcohol has been studied at 25°. The hydrolysis occurs according to the equation $dx/dt = [\text{ester}][NaOH][0.12911(1 - \alpha) + 0.05710\alpha]$, in which α is the degree of dissociation of the base calculated from the dissociation constant. The undissociated molecules of the base hydrolyse more rapidly than the ions. If all the products remain in solution, the reaction follows the equation for second-order reactions, but with a concentration of sodium hydroxide above 0.38, the reaction takes

place more rapidly than the equation demands. The addition of sodium acetate increases the velocity of the hydrolysis. This depends on the total sodium concentration of the solution. The falling off of the velocity, which, according to the theory, ought to take place on account of the precipitation of sodium acetate, is so small as to be unrecognisable in this case. With increasing water concentration, the velocity increases very rapidly. If the sodium hydroxide solution is prepared by adding sodium to the alcohol, and the water content is so small that the whole of the sodium is not converted into hydroxide, then the velocity is very small and the reaction does not occur according to the equation for reactions of the second order. This is probably because the hydrolysis is effected by the sodium hydroxide, and not by the sodium ethoxide. When sodium hydroxide is dissolved in concentrated methylated spirit, a considerable contraction occurs. Experiments on the water content to determine the equilibrium conditions between alcohol, sodium acetate, and its trihydrate at 25° led to no definite result, but point to the fact that a water content of 4—5% is necessary.

J. F. S.

The Relative Activity of certain Alkyl Iodides with Sodium α -Naphthoxide in Methyl Alcohol. HENRY EDWARD COX (T., 1918, 113, 821—824).

Preparation of Catalytically Active Substances. FRIEDA MULLER (D.R.-P. 307380; from *Chem. Zentr.*, 1918, ii, 492—493). —Werner's salts [that is, the double salts of the heavy metals and complex salts described by Werner (*Neuere Anschauungen auf dem Gebiete der organischen Chemie*, 1913)] are heated with exclusion of air at a temperature not exceeding that at which the catalyst is intended to be used. Heating may occur in a current of nitrogen or in a vacuum; if the product is to be used as catalyst for reaction between gases, the heating may take place in an atmosphere of one or all of the gases. Previous to heating, the substance may be distributed over carriers, such as clay or asbestos. For reactions between liquids and gases, the heating may proceed in the liquid after the salt has been dissolved, suspended, or emulsified. In many cases, it is necessary to heat under pressure. A catalyst from potassium chromicyanide at 300° gave 15% of ammonia at 300° and 120 atmospheres. Ammonia undergoes quantitative combustion in the presence of the product from luteo-chromium ferricyanide at 300°. Ammonium ferrimolybdate when heated at 400° in an atmosphere of nitrogen and hydrogen yields a loose, black powder which yields 19% of ammonia at 160 atm. and 400°. Ammonium sodium cobaltcyanide is converted by ignition at 700° in nitrogen into a very porous, black catalyst for the synthesis of ammonia. Carbonatopentaminocobalt nitrate is heated at 420° in a current of nitrogen and hydrogen for the preparation of a catalyst. Up to 8% of formaldehyde could be

obtained from methane and oxygen at 150° by use of a catalyst from croceocobalt nitrate (heated in nitrogen at 150°). The catalyst from nitratopurpureocobalt nitrate is useful in the synthesis of ammonia. Indole is formed by hydrogenation of methyl *o*-toluidine in the presence of the catalyst from hexaquochromi-acetate. Borneol is converted into camphor in the presence of a product from hexaquochromi-propionate. A catalyst from cobalt hydroxynitrite brings about the quantitative oxidation of sulphur dioxide to sulphur trioxide by an excess of oxygen. H. W.

Hydrogenation and Dehydrogenation of Carbon Compounds with the Aid of Catalysts. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 307580, 307989; from *Chem. Zentr.*, 1918, ii, 573, 693).—The conversion of organic compounds or of oxides of carbon into hydrogenated substances can be effected at relatively very low temperatures if contact agents are used which, in addition to the catalysing metal (metals of the platinum-palladium group are excepted), contain oxides of the earth metals, including the rare earths or of glucinum or magnesium. Satisfactory activation can only be secured by the use of very intimate mixtures. These may be prepared by simultaneous precipitation of the suitable hydroxides, oxides, carbonates, etc., from a solution of mixed salts, by heating mixtures of molten salts, and also, though not always with equal certainty and effect, by mechanical processes, such as very fine grinding, kneading in the moist state, pressing, etc.; when necessary, the mass is subjected to subsequent ignition and reduction. The production of highly active contact agents is greatly facilitated if at any rate the catalysing metal is formed from salts containing carbon, such as carbonates, formates, etc. The activity of the contact agent is frequently increased by adding compounds of the alkali metals, for example, sodium hydroxide, either to the mixture itself or to the materials from which it is prepared, a small quantity being frequently sufficient. It is sometimes advisable to add other organic or inorganic materials as carriers or binding material, or for the purpose of increasing the porosity of the mass; in such cases, the introduction of substances which, like chlorine, sulphur, phosphorus, and arsenic, can act as poisons, is best avoided. If reduction to the metallic state is necessary, it should be effected at as low a temperature as possible by pure hydrogen or other suitable agent. The catalytic activity of nickel, cobalt, and iron is particularly increased. The preparation of catalysts for the conversion of carbon dioxide into methane, the hydrogenation of oils, and the reduction of nitrobenzene is described.

The second patent describes the use of other difficultly reducible oxides of high melting point, particularly those of titanium, uranium, manganese, vanadium, columbium, or tantalum, in place of the oxides previously cited. Examples are given of the hydrogenation of cotton-seed oil and the hardening of earth-nut oil at 100 — 120° . H. W.

Negative Catalysts in the Hydrogenation of Oils.

SEIICHI UENO (*J. Chem. Ind., Tokyo*, 1918, **21**, 898—939).—The degree of the hydrogenation of oils may be indicated by the formula $r = x/a$, where r represents the "ratio number of hydrogenation," x the difference between the iodine values before and after hydrogenation, and a the original iodine value of the oil. A comparison between the values of r and r' (the ratio number of hydrogenation in the absence of the particular substance) will show whether or no any given substance acts as a negative catalyst. By this means, various typical substances have been classified in accordance with their action on the catalytic hydrogenation of oils in presence of a nickel catalyst. Certain metallic soaps, such as those of potassium, barium, zinc, cadmium, lead, uranium, and gold, are injurious, whilst others, including those of calcium, aluminium, cerium, nickel, thorium, and platinum have no effect. Nickel salts of simple monocarboxylic acids, nickel lactate, and nickel salts of dicarboxylic acids (oxalic and succinic acids) have also no influence on the results. Copper hydroxide acts as a negative catalyst, but nickel hydroxide does not. Ammonium molybdate, boric acid, hydrochloric acid, and potassium hydroxide are pronounced poisons. Fatty acids, such as acetic, stearic, and oleic acids, have no effect, but hydroxystearic acids act as poisons, as do also hydroxy-acids, such as malic, citric, and tartaric acids. Certain powdered metals, such as tin, zirconium, and aluminium, have no marked action, but others, such as iron, lead, and zinc, are slightly poisonous. Other negative catalysts include sulphur, selenium, and tellurium, red phosphorus, glycerol, lecithin, alkaloids such as morphine and strychnine, potassium cyanide, and amygdalin. [See also *J. Soc. Chem. Ind.*, 1919, 20A.] C. A. M.

Catalytic Scission of Carbon Dioxide from Keto-carboxylic Acids.

G. BREDIG and R. A. JOYNER (*Zeitsch. Elektrochem.*, 1918, **24**, 285—298).—The rate of decomposition of camphorcarboxylic acid into carbon dioxide and camphor by the bases quinoline, 2-methylquinoline, α -picoline, s -collidine, piperidine, pyridine, dimethylaniline, tribenzylamine, benzyldiethylamine, benzylamine, allylamine, triisobutylamine, diisobutylamine, isoamylamine, tripropylamine, and diethylamine has been determined in the solvents acetophenone, o -nitrotoluene, and m -xylene. The reactions were carried out at 80.2° , and the rate was determined by weighing the carbon dioxide evolved. A series of determinations made to ascertain the equilibrium between acid and the various bases in m -xylene solution is described. These were carried out at 20.1° . A series of molecular weight determinations of the piperidine salts of a number of acids in benzene and ethyl alcohol solutions is also described. It is shown that the rate of decomposition of camphorcarboxylic acid in xylene, acetophenone, and o -nitrotoluene is practically the same in all cases, but in alcohol and water the decomposition is much slower. There is no direct connexion between the affinity constants of the

bases in water and the velocity of decomposition in the above-named solvents. The action of bases on the optical rotation of camphorcarboxylic acid was investigated, and it is shown that in *m*-xylene solution the simple Oudemann law does not hold, but in some cases the extent to which the salt is split up into acid and base can be determined. In *m*-xylene solution, the bases form acid complexes with an excess of the acid, in which more than one molecule of acid is combined with one molecule of base. In the extreme case, three molecules of acid are combined with one molecule of base. The velocity of decomposition of the salts is shown in the case of a series of bases to be parallel with the number of molecules of acid which combine with one molecule of base. It is probable that every carboxylic acid forms acid complexes with bases, but picric acid does not do so. Association of the acids only occurs in those solvents in which acid complexes with bases are formed, and the catalytic decomposition of camphorcarboxylic acid only occurs in those solvents in which acid complex formation takes place between the acid and base.

J. F. S.

The Hydrolysis of Soap Solutions, Measured by the Rate of Catalysis of Nitrosotriacetoneamine. JAMES WILLIAM McBAIN and THOMAS ROBERT BOLAM (*T.*, 1918, **113**, 825—832).

Mercury as a Contact Poison. G. BREDIG (*Ber.*, 1918, **51**, 1477).—The poisoning of catalysts by mercury (compare Paal and Hartmann, *A.*, 1918, ii, 303) has been previously noticed by Bredig and Berneck (*A.*, 1900, ii, 213) and others.

C. S.

Whole Number Atomic Weights and Related Questions. R. VON MISES (*Physikal. Zeitsch.*, 1918, **19**, 490—500).—A mathematical paper in which the probability that the atomic weights are whole numbers is treated.

J. F. S.

The Atom Model of Bohr. ARTHUR SZARVASSI (*Physikal. Zeitsch.*, 1918, **19**, 504—508).—A mathematical paper in which an attempt is made to explain certain insufficiently defined points in the theory of the structure of the atom as put forward by Bohr.

J. F. S.

Atomic Structure. P. DEBYE and P. SCHERRER (*Physikal. Zeitsch.*, 1918, **19**, 474—483).—A theoretical paper in which the rôle of the electron rings in the structure of crystals is discussed. It is shown that the electron rings of the carbon atom do not act as bonds in the structure of the diamond. The number of electrons accompanying the atoms in compounds is discussed, and some calculations are carried out in this connexion. The dimensions of the electron rings of the atoms are considered, and a method is worked out for calculating this quantity. Thus for the diamond it is shown that the radius of the electron ring is 0.43×10^{-8} cm., a figure which is in keeping with the value calculated by Bohr for

a ring in which four electrons are travelling round a nucleus containing four charges. In this case, the value is 0.17×10^{-8} cm.

J. F. S.

Theory of Röntgen Spectra. FRITZ REICHE and ADOLF SMEKAL (*Ann. Physik.*, 1918, [iv], **57**, 124—144).—A theoretical paper in which the relative positions of the *K* and *L* electron rings are discussed. Assuming the hypothesis of Debye and Vegard, and neglecting the electric and magnetic disturbances between the *K* and *L* rings, the formula $\Delta = v_{La}/R - 5/36z^2 = B_{p_1p_2} \cdot z + C_{p_1p_2}$ is deduced. In this equation, v_{La} is the vibration number of the *L_a* line, *R* the Rydberg number, *z* the atomic number of the element, $B_{p_1p_2}$ and $C_{p_1p_2}$ are functions of p_1 and p_2 , the number of electrons in the *K* and *L* rings respectively. The values of v_{La}/R and $5/36z^2$ are evaluated for the elements of atomic numbers 30—92, and it is shown that up to 58 the agreement is linear, and above this number the divergence is very small, so that it becomes necessary to take the disturbances into account in such calculations.

J. F. S.

Coupling of Electron Rings and Optical Activity of Asymmetric Molecules. A. LANDÉ (*Physikal. Zeitsch.*, 1918, **19**, 500—504).—A mathematical paper in which the connexion between the optical activity of asymmetric molecules and the electron rings is treated.

J. F. S.

Systematic Valency Theory and the Explanation on this Theory of Complex Compounds. Ionogen and Labile Bonds, Gaseous Molecules, Polymerisation and Isomerisation. EMIL KOHLWEILER (*Zeitsch. physikal. Chem.*, 1918, **93**, 113—153).—A continuation of the work previously published (A., 1918, ii, 304).—It is shown in the present paper that the views put forward to explain the formation and stability of compounds of the first order are equally applicable to compounds of higher orders. Particularly it is shown that the mechanism of the formation of molecular and complex compounds is the same as that of simple compounds in respect of the method of linking. The origin of ionogen and non-ionogen bands, polymerisation and isomerisation, the constitution of explosives and unstable compounds, and that of the gaseous molecules, are explained on the basis of this theory. For details of these points the original paper should be consulted.

J. F. S.

Apparatus for Facilitating the Manipulation of Gases. MAX BODENSTEIN (*Ber.*, 1918, **51**, 1640—1645).—(1) A vacuum tube opener similar to that described by Stock (A., 1918, ii, 353) has been used by the author for more than twenty years. (2) A stopcock is described the extremities of the stopper of which are surrounded by the gas under manipulation, so that the intrusion of air is impossible. (3) A mercury gasometer is described which

requires the use of very little mercury. (4) A fatless metallic stopcock and (5) a quartz Bourdon manometer are also described. The first three pieces of apparatus are figured. C. S.

Condenser. R. HOWDEN (*Chem. News*, 1918, **117**, 368).—The apparatus consists of a test-tube 2.5 cm. in diameter and 20 cm. long, which is placed in a vessel through which cold water is circulated. The tube is closed by a cork through which pass the tube from the distillation flask, and a second tube which extends from the bottom of the test-tube, the upper end of this second tube being bent downwards into a receiver. The first portion of the distillate collects in the test-tube; as further quantities collect, the contents of the test-tube are forced over into the receiver. W. P. S.

Two Lecture Experiments. FR. FICHTER (*Helv. Chim. Acta*, 1918, **1**, 430—432).—(1) *Absorption of Gases by Water*.—In demonstrating the absorption of very soluble gases by water, it is usual to collect them over mercury and then to admit water; in order to obtain the gas free from air and to collect over mercury without allowing it to escape into the atmosphere, the author recommends the use of a eudiometer, the upper end of which is drawn out into a tube connected through a stopcock with a T-piece. The eudiometer is filled with mercury up to the stopcock. The gas is then passed through the open limb of the T-piece until a test sample dissolves completely in water; it is then passed into the eudiometer by cautiously opening the cock. The experiment is completed as usual. (2) *Preparation of Calcium Carbide without an Electric Furnace*.—A quantity of compressed carbon dioxide snow is placed on an iron dish and covered with finely divided calcium mixed with loose solid carbon dioxide; reaction is started by allowing burning calcium to fall on the mixture, and proceeds vigorously. The presence of calcium carbide and nitride is demonstrated in the usual manner. Formation of the latter is inhibited as far as possible by using a considerable excess of carbon dioxide. The calcium must be in a finely divided state; large pieces only react superficially, and the presence of free calcium in the product causes the acetylene evolved, on addition of water, to be so largely diluted with hydrogen that it does not give a smoky flame. H. W.

Inorganic Chemistry.

The Determination of the Molecular Complexity of Liquid Sulphur. ALEX. MITCHELL KELLAS (T., 1918, 113, 903—922).

Occurrence of Hydrogen Selenide in Rain and Snow. P. KARRER (*Helv. Chim. Acta*, 1918, 1, 499).—Repetition of Gassmann's experiments (A., 1918, ii, 309) has led the author to the conclusion that selenium is not present in snow or rain. H. W.

Starting and Stability Phenomena of the Oxidation of Ammonia and Similar Reactions. F. G. LILJENROTH (*Chem. and Met. Eng.*, 1918, 19, 287—293).—Conversion curves have been plotted for the oxidation of ammonia at various temperatures, showing that whilst little oxidation takes place at 400°, it rises rapidly between 450° and 500° to nearly 100%, reaches a maximum at about 750°, and then decreases first slowly and afterwards rapidly. The temperature of the gauze or catalyst may also be plotted for various percentages of ammonia-oxidation, and the curve is found to be a straight line, the position of the line, termed the "heat of reaction line," on the conversion curve diagram depending on (1) the initial temperature of the gas, and (2) the initial composition of the gas. The effects of changes in the velocity and the composition of the gaseous mixture on the relative positions of these two curves are described, and the conditions for (1) the cessation of the reaction, (2) overcoming the prejudicial effects of catalytic poisons, are indicated. The reaction does not start spontaneously, but must be initiated by heating to a particular ignition temperature, which is below the reaction temperature. The use of oxygen is shown to be not justified, as it merely results in a higher temperature, necessitating water cooling of the gauze. A cheap low-grade catalyst may be possible for the first gauze, and a platinum gauze for completion of the oxidation in a manner analogous to the sulphuric acid process. The synthetic ammonia process is also considered, and it is shown that in this case a heat exchanger must always be used, and additional heat must usually be supplied. With a high pressure and a good catalyst, however, no heat need be supplied except during the starting period.

B. N.

The Oxidation and Ignition of Coal. RICHARD VERNON WHEELER (T., 1918, 113, 945—955).

Oxidation of Carbon Monoxide in Contact with Copper. K. A. HOFMANN (*Ber.*, 1918, 51, 1334—1346).—Continuing his search for a reagent to oxidise carbon monoxide at the ordinary temperature (A., 1916, ii, 637), the author has shown that hydrated

copper oxide in the presence of aqueous alkali converts carbon monoxide into a carbonate, although at only a slow rate. The addition of platinum metals, especially iridium, increases the rate five times. In contact with metallic copper moistened with aqueous alkali carbon monoxide mixed with air is oxidised two or three times more rapidly than it is when in contact with a copper oxide surface of the same area. The copper is converted into a peroxide, Cu_2O_3 or CuO_2 , which is the real oxidising agent. The addition of a trace of iridium to the copper does not change the oxidising power of the peroxide, but increases the adsorptive capacity of the surface for carbon monoxide, and thus increases the rate of oxidation. It is very remarkable that the rate of oxidation of hydrogen in contact with an alkaline copper surface is only $1/70$ (with addition of iridium, $1/50$) of that of carbon monoxide, the copper surface having a very small capacity of adsorbing molecular hydrogen. The experiments were performed in a Hempel gas pipette filled with rolls of copper gauze moistened with 15% potassium hydroxide solution. The concentration of the alkali does not appreciably affect the results. C. S.

The Action of Chlorine on the Alkali Iodides. WILLIAM NORMAN RAE (T., 1918, 113, 880—884).

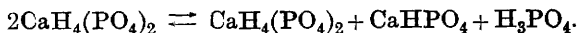
Literature on the Solubility of Systems Relating to Nitre Cake. H. W. FOOTE (*J. Ind. Eng. Chem.*, 1918, 10, 896—897).—A resumé of the literature dealing with the solubility relationships of the systems, $\text{Na}_2\text{SO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$; $\text{Na}_2\text{SO}_4\text{--RSO}_4\text{--H}_2\text{O}$; and $\text{RSO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$ ($\text{R}=\text{Fe}''$, Cu, Ba, Ca, Gl, etc.). J. F. S.

Recrystallisation of Nitre Cake. BLAIR SAXTON (*J. Ind. Eng. Chem.*, 1918, 10, 897—901).—Equations, based on solubility determinations, have been developed, by means of which the amount of any one solid phase, that can be separated from the system $\text{Na}_2\text{SO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$, can be calculated if the composition of the original nitre cake and the acid concentration after crystallisation are known. These equations are for the temperature 25° . Further equations are given for the same temperature, by means of which the amount of water to be added to the nitre cake may be calculated in order to leave a calculated amount of one of the solid phases. Further equations for obtaining the maximum amount of each solid phase from solution at temperatures of 0° and 25° are also given. Leaching processes are outlined, by means of which sulphuric acid may be concentrated in the solution and sodium sulphate in the solid. It is found experimentally that this separation can be carried out more efficiently at 0° than at 25° . J. F. S.

Colloidal Silver. ALWYN PICKLES (*Chem. News*, 1918, 117, 358).—When well-washed silver oxide is reduced by a rapidly stirred 30% solution of formaldehyde, a solution of colloidal silver is produced. This solution is very stable, and varies in colour from pale

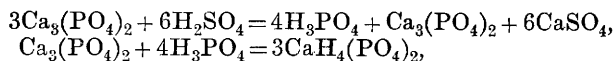
lilac to rich ruby-red. Acetaldehyde has not the same effect, and with formaldehyde the coloured solutions are only produced at about 35°. The colour is discharged slowly by salt solutions, and by nitric acid. Hydrogen peroxide is slowly decomposed by the solution. J. F. S.

Rational Preparation of Superphosphates. A. AITA (*Annali Chim. Appl.*, 1918, 10, 45—103).—On dissolving increasing quantities of monocalcium phosphate in a given weight of water at constant temperature the proportion of free phosphoric acid continually increases, and tends towards a limit in accordance with the equation

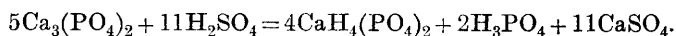


Up to the saturation point at 15° there would thus be a liquid phase consisting of water, monocalcium phosphate, and free phosphoric acid, and a solid phase consisting solely of dicalcium phosphate formed by hydrolysis of the monocalcium phosphate. Beyond the saturation point, with increasing quantities of calcium oxide and phosphoric oxide, the liquid phase remains unaltered, whilst the solid phase is constantly enriched by monocalcium phosphate. On raising the temperature the decomposition of the monocalcium phosphate is accentuated, whilst the saturation point is retarded. Monocalcium phosphate appears in the solid phase at the same limit of concentration for the calcium oxide, but at a greater concentration of the phosphoric oxide. In the case of commercial superphosphates containing about 12—20% of soluble phosphoric oxide and 10—20% of water, there is a system with a fairly high proportion of phosphoric oxide, and a very low proportion of water. In estimating free phosphoric acid in such products it is necessary to use anhydrous ether for the extraction, since water, alcohol, or ordinary ether cause more or less hydrolysis of the monocalcium phosphate, according to the amount of water originally present. The physico-mechanical properties of superphosphates depend on the proportion of free phosphoric acid and water, the former depending on the nature and physical conditions of the components of the reaction, and the latter mainly on the concentration of the sulphuric acid used in the preparation. On these grounds commercial superphosphates may be classified as *normal* or *abnormal* products, the former containing not more than 10—12% of water or 1—2% of phosphoric oxide as free phosphoric acid (about 5—10% of the total soluble phosphoric oxide). Dicalcium phosphate is invariably present, and the fraction of phosphoric oxide in that form of combination should be equal to that present as free phosphoric acid. The mono- and di-calcium phosphates and calcium sulphate are mainly present in the hydrated form. In the case of superphosphates of abnormal constitution the water of the liquid phase exceeds 12%, and the free phosphoric acid exceeds 2% or 10% of the soluble phosphoric oxide, whilst the salts are mainly in the crystalline condition, and there is little or no dicalcium phosphate present. It is commonly

accepted, in accordance with Kolb's view, that the reaction between sulphuric acid and mineral phosphates takes place in two stages:



but the observed facts show that the main reaction is more correctly represented by the equation:



The influence of raising the temperature on the reaction is to increase the concentration of free phosphoric acid in the liquid phase, whilst in the solid phase the dicalcium phosphate increases in equal proportion with the free phosphoric acid. These constituents gradually interact to form monocalcium phosphate, so that the existence of dicalcium phosphate in an industrial product will depend on the proportion of free phosphoric acid originally present. Hence in products prepared with an excessive quantity of sulphuric acid, and thus containing a high proportion of free phosphoric acid, the dicalcium phosphate will be reduced or disappear altogether. In fact, monocalcium phosphate is not hydrolysed in presence of an excess of phosphoric acid, and in such cases the solid phase of the system will consist solely of monocalcium phosphate. The application of these principles to the industrial preparation of superphosphates yields products with the desired physico-mechanical properties. [See also *J. Soc. Chem. Ind.*, 1919, 23A.] C. A. M.

The Decomposition of Barium Peroxide and the Reactivity of the Resulting Barium Oxide. J. ARVID HEDVALL (*Zeitsch. anorg. Chem.*, 1918, **104**, 163—168).—The decomposition of barium peroxide by heat at atmospheric pressure has been followed by means of the heating curve. The peroxide was heated in a carbon tube furnace and the temperature recorded at 10 sec. intervals by means of a platinum—platinum—rhodium thermoelement. The reaction being endothermic, its range is indicated on the heating curve by a pronounced flattening towards the time axis. The temperature at which the vapour pressure of the evolved oxygen is equal to 760 mm. was found to be 795°. This agrees with the value 796° found by Le Chatelier. The higher temperature, 825°, obtained by Hildebrand is accounted for by the fact that this observer used very carefully dried materials, for in the absence of moisture the reaction is very slow and incomplete.

In presence of copper oxide, barium peroxide starts to decompose at about 200°, the reaction becoming most vigorous at 625—660°. as shown by the heating curve. When the peroxide is heated with amorphous silica, however, the rate of rise of temperature increases above 400°. The endothermic decomposition of the peroxide is evidently accompanied by a more strongly exothermic reaction, probably the formation of a barium silicate, brought about by the great reactivity of the barium oxide at the moment of its formation. Even when powdered quartz glass or crushed quartz is used

in place of amorphous silica, there is evidence in the heating curve of silicate formation. E. H. R.

Solubility of Cupric Hydroxide, to a Certain Concentration in Sodium Hydroxide and Potassium Hydroxide. ED. JUSTIN-MUELLER (*Compt. rend.*, 1918, **167**, 779—780).—Cupric hydroxide dissolves in aqueous sodium hydroxide (D 1.345—1.370) or aqueous potassium hydroxide (D 1.453—1.498) to the extent of 0.78 gram in 100 c.c., giving bright blue solutions which do not give any precipitate when boiled directly or first diluted and then boiled. Solutions prepared with more dilute alkali are not stable.

W. G.

Scandium from a Brazilian Source. C. JAMES (*J. Amer. Chem. Soc.*, 1918, **40**, 1674).—Whilst working up quantities of Brazilian zirconia the author obtained a gelatinous residue which on examination was shown to consist of scandium fluoride.

J. F. S.

Rare Earths. VIII. Separation of Yttrium from Erbium ; The Ratio $\text{Er}_2\text{O}_3 : 2\text{ErCl}_3$. EDWARD WICHES, R. S. HOPKINS, and C. W. BALKE (*J. Amer. Chem. Soc.*, 1918, **40**, 1615—1619. Compare A., 1917, ii, 34).—Using material containing only erbium and yttrium, the authors have investigated the newer methods proposed for the separation of these two elements. The cobalticyanide and the nitrite precipitation methods were found to give good results, the latter being the more efficient and practicable. The older nitrate fusion method was found to give results far superior to the other methods, and by this method erbium compounds of a high degree of purity were obtained. The ratio of erbium oxide to erbium chloride was determined in seven analyses. The ratio was found to vary with the temperature and length of time of ignition of the oxide. Erbium oxide, prepared by the ignition of the oxalate and ignited for several hours at 800° and two hours at 900°, was found to retain considerable amounts of carbon dioxide. This is contrary to Hofmann's results (A., 1910, ii, 1073), and consequently brings into disrepute the present accepted value of the atomic weight of erbium. Until erbium oxide of the definite composition Er_2O_3 is prepared, no ratio in which the oxide is one term can be trustworthy for the purpose of atomic weight determinations.

J. F. S.

Preparation and Properties of Yttrium Mixed Metal. J. F. G. HICKS (*J. Amer. Chem. Soc.*, 1918, **40**, 1619—1626).—Experiments of a preliminary nature dealing with the preparation of yttrium mixed metal are described. It is shown that the method of preparing anhydrous chlorides of the metals of the yttrium earths, by heating the hydrated chlorides with ammonium chloride to drive off five of the six molecules of water of crystallisation, and then in a current of hydrogen chloride to remove the

last molecule of water, is capable of being used on the large scale. The mixed metal has been prepared in the form of powder by heating the anhydrous chlorides with sodium in a vacuum at 1100° , and also by electrolysing a mixture of the molten chlorides in a protected graphite crucible, using a graphite anode. Electrolysis of a solution of the mixed oxides in fused cryolite also yields the mixed metal in the form of powder, but the method is less efficient than the foregoing methods. In all these processes, there is considerable loss of yttrium chloride, owing to its volatility at the temperature of the experiments. The powdered products have been obtained in a coherent form by sintering in a vacuum, but the resulting mass easily disintegrates. The product obtained has a mean "atomic weight" of 120 and contains 94.05—95.70% of metal, which corresponds with 37.5% of yttrium. It burns in the air at a dull red heat with a very bright light, and yields a light brown oxide. It is slowly oxidised by moist air at the ordinary temperature. It glows when heated in hydrogen, nitrogen, or carbon dioxide. It does not amalgamate with mercury, and is readily attacked by water. Yttrium mixed metal is pyrophoric, but not so strongly as the cerium metal iron alloys. J. F. S.

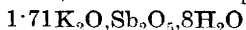
Effects of Heat on Chemical Glassware. R. G. SHERWOOD (*J. Amer. Chem. Soc.*, 1918, **40**, 1645—1653).—When glass is heated, there is shown to be evidence of two distinct kinds of gaseous evolution, that resulting from adsorbed material, which is readily removed at temperatures below 300° , and that resulting, in all probability, from a decomposition of the glass itself. The latter effect becomes important above 400° for the softer glasses and above 500° for the harder glasses. There is some evidence of a definite characteristic rate of gaseous evolution for each temperature to which glass is subjected, increasing with the temperature and extending over a considerable period. Observations on one sample at 500° showed a small, continuous evolution even after heating for twenty hours. Adsorption products are confined to quantities which are represented approximately by a layer of gas about one molecule deep, and are removed with much greater rapidity at lower temperatures than the other products obtained, which are due to the heating of the glass. The most important of the gaseous evolution products obtained from glass under the influence of heat is water, which, as the temperature is raised to the softening point of the glass, constitutes almost the entire quantity of the evolution, but its amount at a lower temperature may be relatively unimportant. J. F. S.

Plasticity and 'Strength' of Clay. OTTO NOLTE (*Bied. Zentr.*, 1918, **47**, 108—109).—Extraction of a heavy Silesian clay with alcohol and ether did not cause any diminution in the plasticity or 'strength' of the clay. The presence of a certain proportion of organic matter, therefore, does not affect these qualities of the clay. The extract was found to contain sulphur and an organic compound which was not identified. H. W. B.

Zirconyl Basic Chromate. F. P. VENABLE and L. V. GILES (*J. Amer. Chem. Soc.*, 1918, **40**, 1653—1656).—A basic zirconium chromate is prepared as a granular, yellow precipitate by dissolving zirconium hydroxide in a boiling solution of chromic acid, diluting, and again boiling the solution. The compound obtained loses a considerable quantity of its water at 110° , but the whole of it is only lost at 200° . The compound is shown to have the formula $2\text{ZrO}(\text{OH})_2 \cdot \text{ZrOCrO}_4 \cdot 8\text{H}_2\text{O}$, and it is suggested that its formation occurs as follows: first, normal zirconium chromate is formed, which is immediately hydrolysed to ZrOCrO_4 ; some of the zirconium hydroxide is partly dehydrated to give $\text{ZrO}(\text{OH})_2$. These two substances then combine to give the yellow, insoluble compound described above. The present work is at variance with earlier work on zirconium basic chromates by Haber (A., 1897, ii, 295).

J. F. S.

Antimonic Acids and Antimonates. GERHARDT JANDER (*Kolloid Zeitsch.*, 1918, **23**, 122—144).—Analyses of the various hydrates of antimony pentoxide have been made, and the dehydration curves of these compounds obtained by keeping them over sulphuric acid in a desiccator. The behaviour of the antimonic acids toward hydrochloric and sulphuric acids and toward solutions of potassium and sodium hydroxides has been studied. The potassium and sodium salts of these acids have also been investigated. The experiments show that the properties of the antimonic acids vary with the method of preparation and with previous treatment. Thus, modifications which differ in their water content, stability, solubility, and their behaviour towards acids and alkalis are obtained (i) by the action of water on the pentachloride, (ii) by the action of acids on antimonates, and (iii) by the hydrolysis of the trichloride in the presence of nitric acid. These varieties of antimonic acid differ only slightly from one another, and probably, as in the case of the stannic acids, the difference is due to a difference in the size of the particles. The experiments indicate that the tri- and tetra-antimonic acids, that is, the soluble antimonic acids, are hydrosols of small stability, and that the definite hydrates of antimony pentoxide known as ortho, pyro-, and meta-antimonic acid can have no free existence. The hydrates of antimony pentoxide exhibit a marked selective absorption towards dilute alkalis. Thereby are formed amorphous substances, which apparently are alkali antimonates. The composition of these substances, however, varies continuously with the composition of the solid hydrate. In concentrated alkali solutions, the hydrates of antimony pentoxide dissolve, and from these solutions at low temperature and by careful evaporation, various alkali antimonates may be crystallised, but the nature of the salt depends on the concentration of the mother liquor. The compound



has been obtained in this way.

J. F. S.

Bismuth Hydride. FRITZ PANETH (*Zeitsch. Elektrochem.*, 1918, **24**, 298—299).—Working from the point of view that isotopes and their compounds are identical, the author is of the opinion that bismuth hydride is capable of existence, and that it is gaseous and only moderately stable, much less so than antimony hydride. These statements are based on the fact that by the action of hydrochloric acid on magnesium which has been covered with thorium-C (an isotope of bismuth), a radioactive hydride is produced which has the properties enumerated above. J. F. S.

Hydroxylamine Platinum Bases. LEO ALEXANDROWITSCH TSCHUGAEV and ILJA ILJITSCH TSCHERNJAEV (*T.*, 1918, **113**, 884—897).

Mineralogical Chemistry.

"Hydromagnocalcite" from the Tatra Mountains, Carpathians. EMANUEL GLATZEL (*Centr. Min.*, 1918, 307—311).—The compact, chalk-white material with conchoidal fracture is found as loose blocks in the Lopusna valley, near the village of Lucivna, on the southern slopes of the Tatra Mountains. Analysis gave results approximating to the formula $\text{CaCO}_3 + \text{Mg}(\text{OH})_2$.

CaO.	MgO.	CO ₂ .	H ₂ O.	Total.	Sp. gr.
36.55	23.15	28.75	10.60	99.05	2.412

[This is evidently penicatite, which was long ago proved to be a mechanical mixture of calcite and brucite ($\text{Mg}[\text{OH}]_2$).]

L. J. S.

Analytical Chemistry.

Quantitative Analysis of Small Quantities of Gases. H. M. RYDER (*J. Amer. Chem. Soc.*, 1918, **40**, 1656—1662).—A somewhat complicated apparatus is described by means of which a quantitative analysis of 5 cu. mm.—1 c.c. of a gaseous mixture of water vapour, carbon dioxide, carbon monoxide, oxygen, hydrogen, nitrogen, and methane may be carried out with an accuracy of about 5% for each constituent. The apparatus makes use of a McLeod gauge and an optical lever gauge, but for details the original should be consulted. J. F. S.

Gas Bubbler for Gas Analysis. OLIVER D. BURKE (*Chem. News*, 1918, **117**, 368—369).—The glass tube through which the

gas enters is drawn out into a fine capillary. Another glass tube is fused on to the side of the first tube and bent so that the end extends just below the end of the capillary, where it is flattened and the top surface ground. The capillary is made to fit tightly on the ground surface, so that the gas escaping from the capillary is broken up into very fine bubbles. [See, further, *J. Soc. Chem. Ind.*, January, 1919.] W. P. S.

Oxidising Action of Potassium Dichromate as Compared with that of Pure Iodine. CARL R. McCROSKEY (*J. Amer. Chem. Soc.*, 1918, **40**, 1662—1674).—The author has studied the trustworthiness of potassium dichromate as a standardising agent in iodometric determinations. It is shown that potassium dichromate always liberates more than the theoretical quantity of iodine from hydriodic acid. This excess of iodine may be reduced, but not wholly removed, by removing dissolved air from the solutions, by drying, and fusing the dichromate in the absence of air and by recrystallising repeatedly to remove oxidising impurities. It is also shown that the excess of iodine is not due in any way to the catalytic action of chromium chloride. J. F. S.

Estimation of Active Oxygen in Sodium Peroxide. JAROSLAV MILBAUER (*J. pr. Chem.*, 1918, [ii], **98**, 1—8).—The following methods have been proposed for the estimation of active oxygen in sodium peroxide: (1) liberation of hydrogen peroxide by water followed by titration with potassium permanganate, (2) treatment of sodium peroxide with potassium iodide and potassium hydrogen carbonate, and titration of the iodine liberated with sodium arsenite, and (3) measurement of the oxygen liberated by water in the presence of cobalt nitrate. The results obtained by the first method are very low, those by the second are somewhat better, but still low, whilst the third method gives high results. The methods have been critically examined and improved; the following processes yield accurate results: (1) Water (100 c.c.) is mixed with concentrated sulphuric acid (5 c.c.) and chemically pure boric acid (5 grams); sodium peroxide (0.5 gram) is gradually added to the mixture, which is kept briskly shaken, and the liberated hydrogen peroxide is titrated with potassium permanganate. The usual permanganate method gives low results, since a portion of the hydrogen peroxide is catalytically decomposed by the manganese sulphate formed during the process. (2) Sodium peroxide is gradually introduced into a solution of potassium iodide (2 grams) in dilute sulphuric acid (1 in 20; 200 c.c.); the iodine is titrated with standard thiosulphate. The results agree fully with those obtained by the permanganate method. (3) Sodium peroxide (0.2—0.3 gram) is mixed with about 10 c.c. of copper sulphate solution (0.05%) in a small flask connected to a nitrometer; the flask is shaken, and decomposition is complete within a minute, when the liberated oxygen is measured. The gas evolved contains about 0.32% of carbon dioxide and 0.08% of

hydrogen. With cobalt nitrate as catalyst, the results are invariably high; the authors consider this may indicate the presence of an oxide higher than the peroxide.

The action of the atmosphere on sodium peroxide has also been investigated; moisture appears to be more active than carbon dioxide in causing decomposition. H. W.

Pregl's Micro-estimation of Nitrogen. HANS FISCHER (*Ber.*, 1918, 51, 1322—1325).—The estimation of nitrogen in difficultly combustible substances by the micro-Dumas method (compare Dubsy, A., 1918, ii, 130) gives untrustworthy results, and the author now employs only the original Pregl method. The causes of the inaccuracies in the former method are discussed.

The author uses the micro-Pregl method in preference to the Lassaigne test for the detection of nitrogen in rare or very valuable organic compounds. C. S.

Detection and Estimation of Hydrogen Phosphide in Hydrogen. J. SOYER (*Ann. Chim. anal.*, 1918, 23, 221—225).—Hydrogen prepared by the action of sodium hydroxide on ferro-silicon always contains traces of hydrogen phosphide. The presence of the latter may be detected by burning the hydrogen from a platinum jet and directing the flame on to the edge of a porcelain basin; the flame has a green coloration. When examined with the spectroscope, the flame exhibits the phosphorus spectrum. If a drop of water suspended on a glass rod is held in the flame for fifteen seconds and then tested with molybdic acid reagent, a yellow precipitate is obtained. The amount of hydrogen phosphide present is estimated by passing a definite volume (from 2 to 20 litres) of the gas, together with a large excess of air, through a platinum jet arranged in a silicon tube heated to bright redness; this tube is inclined slightly, and its lower end is connected with absorption vessels containing water. When the desired quantity of the gas has been burned, the tube and the contents of the absorption vessels are rinsed into a basin, treated with 5 grams of ammonium nitrate, concentrated to about 40 c.c., and the phosphoric acid precipitated with molybdic acid reagent. [See, further, *J. Soc. Chem. Ind.*, 1918, 765A.] W. P. S.

Estimation of Minute Quantities of Arsenic. O. BILLETER (*Helv. Chim. Acta*, 1918, 1, 475—498).—A more extended and somewhat modified account of the method previously published (*A.*, 1915, ii, 578).

The estimation of arsenic in organic substances is effected in the following manner. The organic matter is destroyed either by treatment with a mixture of nitric and concentrated sulphuric acids or, in the case of urines, by rendering the latter alkaline with sodium carbonate, evaporation to a syrup, admixture with potassium perchlorate (2 grams) and potassium sulphate (4 grams) for each 100 c.c. of urine, desiccation of the mixture at 120°, and

gradual introduction of the latter into a platinum crucible heated to dull redness, followed by more intense ignition until tranquil fusion is attained. The arsenic is separated from other metals by distillation with a mixture of sodium chloride (2 grams) and potassium bromide (0.2 gram) for each 20 c.c. of sulphuric acid (the addition of hydrazine sulphate previously recommended is found to be unnecessary), or, if destruction of organic matter has been effected with potassium perchlorate, by treatment with potassium bromide (0.1—0.2 gram) and sulphuric acid (90%, 6 c.c.). Mercury is completely retained by one distillation, but if antimony is present, it is necessary to redistil after addition of 5—6 grams of sulphuric acid (90%). Hydrochloric acid is eliminated from the distillate by treatment with hypochlorous acid, and the solution is evaporated to dryness. The residue is dissolved in sulphuric acid (12%, 1 c.c.) and evaporated on the water-bath to destroy any chloric acid that may be present; after addition of water (0.85 c.c.), it is transferred to a Marsh's apparatus. By this method, 0.01 mg. of arsenic may be detected.

The precautions necessary for ensuring the requisite purity of the reagents are fully described. The commercial pure sulphuric acid is diluted to 85% and heated with sodium chloride (3%) and potassium bromide (0.3%) in a quartz flask; the treatment is twice repeated with smaller quantities of salts, and the acid is finally distilled from a quartz retort and collected in a quartz flask. The nitric acid and the salts are purified by Lockemann's method. Zinc is conveniently obtained by the electrolysis of an aqueous solution of zinc sulphate, using a zinc anode and copper cathode; the metal is obtained in the pulverulent state, and dissolves readily in dilute sulphuric acid without being activated. It is free from arsenic. Hypochlorous acid is best prepared by the solution of chlorine monoxide in water.

The sensitiveness and constancy of the arsenic mirrors depend considerably on the quality of the calcium chloride used in desiccating the gas. Commercial fused calcium chloride is unsuitable, as it is always strongly alkaline; a neutral product can be obtained by dehydrating the crystalline substance at 200°, and subsequently gradually heating the finely divided product to its melting point in a quartz tube in a slow current of dry hydrogen chloride. The best results are obtained by starting from metallic calcium.

H. W.

Amount of Amorphous Silica in the Soil. BELA VON HORVATH (*Bied. Zentr.*, 1918, **47**, 97—98).—For the estimation of the amorphous silica, 5 grams of the soil are extracted with 100 c.c. of a 1% sodium carbonate solution for fifteen minutes at 100°. Solutions of sodium carbonate of greater concentration than 1% dissolve silicates and quartz besides amorphous silica, the results obtained being consequently too high. When estimated by the author's method, soil is found to contain only a few milligrams per cent. of amorphous silica.

H. W. B.

Estimation of Metals by Electrolytic Deposition without using an External Supply of Electricity. MAURICE FRANÇOIS (*Compt. rend.*, 1918, **167**, 725—727).—A strip of nickel is placed across the top of a platinum crucible, and a zinc rod, 5 mm. in diameter, is suspended from the strip; the rod is notched so as to fit on to the nickel strip, and the lower end of the rod extends nearly to the bottom of the crucible. The zinc rod is amalgamated at least twenty-four hours before being used, and is wrapped in filter-paper, which is tied on to the rod with ordinary cotton thread. The electrolyte used for the deposition of silver or gold consists of 9 c.c. of 10% potassium cyanide solution, 5 c.c. of potassium hydroxide solution (D 1·332), and 2 c.c. of ammonia; for the deposition of mercury, the solution should consist of 20 c.c. of 10% sulphuric acid containing 0·5 gram of potassium iodide. In all cases, the deposition requires twenty-four hours for completion. [See, further, *J. Soc. Chem. Ind.*, 1918, 784A.]

W. P. S.

Quantitative Estimation of Ions by Microanalytical Methods. I. ROBERT STREBINGER (*Österr. Chem. Zeit.*, [ii], **21**, 71—73; from *Chem. Zentr.*, 1918, ii, 471).—The author has extended Pregl's method of quantitative organic micro-analysis to inorganic substances, and describes the estimation of silver, nickel, arsenic, iron, chromium, and copper, and the separations of silver from copper and lead from tin. Precipitation of nickel with α -benzildioxime is unsuitable for micro-analytical purposes, the results being too high. H. W.

Gravimetric Analysis. VI. Estimation of Calcium.
VII. Separation of Calcium from Magnesium. L. W. WINKLER (*Zeitsch. angew. Chem.*, 1918, **31**, 187—188, 203, 214—216).—Estimation of calcium as oxalate or carbonate was submitted to critical examination. It is recommended that the precipitation as oxalate should be made from an acetic acid solution in the presence of ammonium chloride; the calcium oxalate should be weighed as such, since ignition to oxide is less trustworthy, especially in the presence of sulphates. If the latter are present, the oxalate always contains sulphate, but the weight is not affected, since the two have practically identical molecular weights. For the separation of calcium from magnesium, the calcium is precipitated as described from an acetic acid solution; the magnesium is subsequently precipitated as ammonium magnesium phosphate and weighed in this form. [See, further, *J. Soc. Chem. Ind.*, 1919, 29A.] W. P. S.

Estimation of Calcium and Magnesium in different Saline Solutions. E. CANALS (*Bull. Soc. chim.*, 1918, [iv], **23**, 422—430).—The simplest and most satisfactory method of estimating calcium is to precipitate it as oxalate in ammoniacal solution and weigh it as oxide. The method of precipitation as

sulphate and weighing as such is also very exact, providing that numerous precautions are taken. [See, further, *J. Soc. Chem. Ind.*, January, 1919].
W. G.

Sensitiveness of the most usual Tests for Copper.

A. WÖBER (*Osterr. Chem. Zeit.*, [ii], 21, 105—107; from *Chem. Zentr.*, 1918, ii, 560).—The usual tests for the detection of copper have been investigated with respect to sensitiveness with a view to their application in microanalysis; the results are given in the form of a table.
H. W.

Separation of Hydroxides in the Ammonium Sulphide Group.

W. D. TREADWELL (*Schweiz. Chem. Zeit.*, 1918, 2, 59—61, 71—74; from *Chem. Zentr.*, 1918, ii, 663—664).—The separation of bivalent from trivalent metals of the ammonium sulphide group by simple precipitation with dilute ammonia from solutions containing ammonium salts is generally not quantitative. Transitory local excess of the reagent cannot be avoided, and the precipitate then carries down varying amounts of the bivalent metal. The necessary asymptotic approach to the neutral point can be easily attained by leading a current of dilute ammonia (obtained by blowing air through a saturated solution of ammonium chloride in the presence of calcined magnesia) through the solution. Precipitation by the gas has the advantage that it is possible to approach the neutral point with the necessary caution without correspondingly diluting the solution. In the presence of manganese, ammonia should not be added until neutralisation is complete, since the manganese ion is readily oxidised by air in neutral solution and passes into the precipitate; neutrality to litmus is the farthest possible limit. In the separation of chromium and manganese, the latter is always adsorbed by the chromium hydroxide. The hydroxides of the trivalent metals carry down nickel and cobalt more readily than manganese and zinc. The error can be somewhat diminished by precipitating and filtering the main portion of the sesquioxides in distinctly acid solution, and subsequently precipitating the remainder from the filtrate after fresh addition of ammonium salts. The precipitates contain much more basic sulphate than chloride. Precipitates from solutions containing sulphates are more sandy in character and do not adhere to glass; when washed, they lose the sulphate ion and become slimy.

Mercuric oxide is not suitable for the precipitation of the trivalent metals of the ammonium sulphide group as hydroxides. When warmed with dilute ammonium sulphate solution, it only liberates an insufficient quantity of ammonia; addition of ammonium chloride effects an improvement, due to the formation of complex mercury salts. The precipitates are very easily filtered; they are ignited wet, when the admixed mercury compounds are quantitatively volatilised.

For the precipitation of aluminium, chromium, and iron, a

freshly prepared mixture of sodium or potassium nitrite and ammonium chloride is to be preferred to the very unstable ammonium nitrite. The precipitates obtained from solutions of ferric salts by this process are very difficult to filter, and are greatly contaminated with basic salts. The difficulty may be avoided by displacing the nitrous acid from the solution by a current of inert gas at the temperature of the water-bath. The utility of the method is limited owing to the oxidising action of the nitrous fumes.

A portion of the aluminium remains in solution when a dilute solution of aluminium chloride is precipitated by sodium thio-sulphate and boiling is continued until sulphur dioxide is completely expelled; precipitation is still less complete in the case of chromium.

H. W.

Arsenite Titrations of Permanganate Solutions. ALOKE BOSE (*Chem. News*, 1918, **117**, 369—370).—Results of experiments are recorded showing that free nitric acid is not the cause of the abnormally high reducing value of sodium arsenite solution when this is used for the titration of permanganate (compare Ibbotson, A., 1918, ii, 175). The formation of manganic compounds does not seem to be possible. Some complicated reactions may take place during the titration, but it is quite clear, from the results of titrations with ammonium ferrous sulphate solution, that all the manganese is present as permanganate before the titration with arsenite is commenced. [See, further, *J. Soc. Chem. Ind.*, 1919.]

W. P. S.

Separation of Germanium from Arsenic by the Distillation of the Chloride in the Presence of a Chromate. PHILIP E. BROWNING and SEWELL E. SCOTT (*Amer. J. Sci.*, 1918, [iv], **46**, 663—665).—A modification of a method described previously (A., 1917, ii, 546); chromic acid is used to oxidise the arsenic, and the germanium chloride is then distilled from the hydrochloric acid solution. Five c.c. of 10% potassium dichromate solution are sufficient to oxidise 0.25 gram of arsenious acid. A current of carbon dioxide may be passed through the apparatus during the distillation to facilitate the removal of the germanium chloride. If as little as 0.0005 gram of germanium oxide is present, the distillate yields a white precipitate of germanium sulphide on the addition of hydrogen sulphide. [See, further, *J. Soc. Chem. Ind.*, 1918, 785A.]

W. P. S.

The Estimation of Phenol and the Three Isomeric Cresols in Mixtures of these Substances. HARRY MEDFORTH DAWSON and CHRISTOPHER ARCHIBALD MOUNTFORD (*T.*, 1918, **113**, 935—944).

General and Physical Chemistry.

The Optical Behaviour of Water of Crystallisation. KÄTHE BRIEGER (*Ann. Physik*, 1918, [iv], 57, 287—320).—Experiments have been made to compare the reflection intensities of crystals of a number of hydrated salts in the infra-red region, $\lambda = 2.5\text{--}7.0\ \mu$, with that of water. The reflection curve for water shows a well-marked maximum intensity at $\lambda = 3.07\ \mu$, and very similar maxima are found for hydrated crystals (compare Schaefer and Schubert, A., 1916, ii, 505). Of the nine isomorphous alums examined, eight show two maxima in the intensity curves in place of the single water maximum at $3.07\ \mu$, their positions being near $3.02\ \mu$ and $3.51\ \mu$, but differing slightly in the different alums. The curve for caesium alum, however, shows a third maximum, and in this respect is abnormal. The water maximum at $\lambda = 6.22\ \mu$ also becomes doubled in the case of the alums.

As examples of uniaxial crystals, the hexahydrated nickel sulphate and selenate (tetragonal trapezohedral) were examined. In the case of these salts, the water maximum is shifted only slightly. The intensity of the reflection depends on the position of the optic axis relative to the reflecting surface, the water of crystallisation exhibiting dichroism. Similarly in the case of monoclinic crystals of the magnesium sulphate and zinc-ammonium sulphate groups, the reflection properties are closely related to the optical properties, the water being trichroic. It is concluded that the symmetry properties of the water in hydrated salts correspond with the symmetry of the crystals. The bearing of the results on Werner's theory of the constitution of hydrated salts is discussed.

Preliminary experiments with analcime indicate a shift of the water maximum towards the shorter wave-lengths, whilst in every other case the shift is in the other direction. Further experiments may be expected to throw light on the constitution of the zeolites generally, especially with regard to the state of combination of the water which they contain. E. H. R.

Effect of the Electric Field on Spectrum Lines. VII. The Fowler Helium Series. J. STARK, O. HARDTKE, and G. LIEBERT (*Ann. Physik*, 1918, [iv], 56, 569—576. Compare Fowler, A., 1913, ii, 811).—The effect of an electric field on the lines $\lambda 3203$ and $\lambda 2733$ of the Fowler helium series has been studied. The effect is compared with that on the Balmer hydrogen series, and it is shown that both effects are very similar, the lines in both cases being symmetrically resolved into their components. The intensity of the two components is equal. J. F. S.

Effect of an Electric Field on Spectrum Lines. VIII. New Principal Series of Helium Lines which Appear in the Electric Field. J. STARK (*Ann. Physik*, 1918, [iv], 56, 577—588. See preceding abstract).—During an investigation of the influence of an electric field on the helium spectrum, two new

principal series of lines were discovered. The lines of the first of these, the He *I* principal diffused series, are given by the formula $\nu = Ez(u) - Lz(m, d)$. In the electric field, the lines of this series are resolved in such a way that the components do not lie symmetrically, but are displaced about 1 Å. unit in the direction of shorter wave-lengths. The second new series of helium lines, the He *I* sharp series, is represented by the formula $\nu = Ez(h) - Lz(m, s)$. The lines of this series in an electric field were not resolved into several components, but were displaced towards the longer wave-lengths. The He⁺ ion possesses twelve series, which can be arranged in two systems of six series. In each system there are three principal series with the same end-number, and three subsidiary series, also with the same end-number. J. F. S.

Effect of an Electric Field on the Ultra-violet Lines of Helium. G. LIEBERT (*Ann. Physik*, 1918, [iv], 56, 589—609. See preceding abstracts).—The ultra-violet lines of the principal series He *I* are displaced towards the red end of the spectrum under the influence of an electric field. Both the components undergo the same amount of displacement. The lines of the second subsidiary series are displaced without resolution toward the red by an electric field. In this case, the displacement is rather more than the proportional amount. The lines of the principal series He *II* are displaced toward shorter wave-lengths by an electric field. In the case of the third subsidiary series of He *I*, a displacement of the lines toward longer wave-lengths is brought about by an electric field. J. F. S.

A New Helium Series under the Influence of an Electric Field. G. LIEBERT (*Ann. Physik*, 1918, [iv], 56, 610—616).—Corresponding with the third He *I* series, a subsidiary He *II* series becomes visible in a strong electric field, whereas in a weak electric field it has no noticeable intensity. The electric effect on every member of the principal series corresponds with the effect on the similar member of the subsidiary series. The lines of the subsidiary series, like those of the principal series, are displaced toward the shorter wave-lengths. J. F. S.

Spectrum of the Chromosphere. An Eruptive Protuberance of the 6th July, 1917. P. CARRASCO (*Anal. Fis. Quim.*, 1918, 16, 700—706).—A comparison of the author's observations of the chromosphere spectrum with the results of Rowland and of Adams. The presence of the helium series 6678·1, 4922·1, etc., is noted as a characteristic of the spectrum. The helium series 7665·6, 4713·2, etc., was not observed. W. S. M.

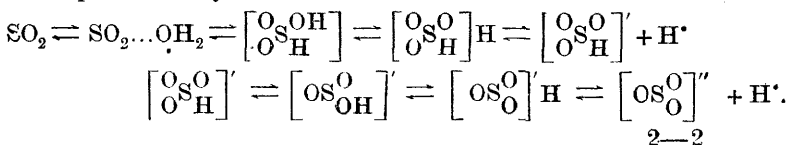
Optical Researches on the Constitution of Sulphurous Acid, its Salts and Esters. KONR. SCHAEFER [with WILLY KÖHLER] (*Zeitsch. anorg. Chem.*, 1918, 104, 212—250).—Aqueous solutions of sulphur dioxide show an absorption band in the ultra-violet in the same position as the band given by sulphur dioxide gas, although somewhat broader. Beer's law is not followed, the

band becoming much shallower with increasing dilution. The absorbing substance in aqueous solutions is a hydrate of sulphur dioxide, $\text{SO}_2 \dots \text{OH}_2$, which appears to be more active than sulphur dioxide itself. Since the normal sulphites and the sulphite esters, $\text{Et} \cdot \text{SO}_2 \cdot \text{OEt}$ and $\text{SO}(\text{OEt})_2$, are both transparent in the ultra-violet, it is concluded that sulphurous acid itself is non-absorbing, both in the unionised and ionised condition. The diminished absorbing power of solutions of sulphur dioxide on dilution is attributed to a change of equilibrium from left to right in the equation $\text{SO}_2 \dots \text{OH}_2 \rightleftharpoons \text{H}_2\text{SO}_3$. The aqueous solution contains very little sulphurous acid, and it is considered that measurements of the ion concentration in sulphur dioxide solutions have given rise to false ideas regarding the degree of dissociation of sulphurous acid, and consequently of the strength of the acid.

At higher temperatures, solutions of sulphur dioxide absorb more strongly, owing to a shift in the equilibrium of the above equation towards the left. Similarly, addition of sulphuric acid to an aqueous solution of the gas increases the depth of the band in the same manner, but only to a certain limit. When the sulphuric acid exceeds 5*N*, the absorption again decreases, probably owing to dehydration, in the sense $\text{SO}_2 \dots \text{OH}_2 \rightarrow \text{SO}_2 + \text{H}_2\text{O}$, the free sulphur dioxide being a less strong absorber than its hydrate. In pentane and chloroform solutions, the absorption is similar to that of the free gas, and the solutions follow Beer's law. In solutions of methyl and ethyl alcohols and ethyl ether, the absorption is much increased, and in the case of ethyl ether the band passes into general absorption in the ultra-violet. These solutions also follow Beer's law, and it is concluded that stable compounds of the type $\text{O}_2\text{S} \dots \text{OHEt}$ and $\text{O}_2\text{S} \dots \text{OEt}_2$ must be present in such solutions.

Normal sulphites show only end absorption in the extreme ultra-violet, and when a solution of a normal sulphite solution is half neutralised with sulphuric acid, the resulting metal hydrogen sulphite solution at first shows only end absorption, but after a few days, particularly under the influence of light, the sulphur dioxide band develops. When the metal hydrogen sulphite is formed, however, by mixing solutions of sulphur dioxide and normal sulphite, the band is present immediately. A solution of potassium pyrosulphite when freshly prepared shows only end absorption in the extreme ultra-violet, but the band gradually develops. Similarly, sodium methyl sulphite, which in methyl alcohol shows only end absorption, in aqueous solution gradually develops the sulphur dioxide band, more quickly in stronger solutions, owing to hydrolysis into sodium hydrogen sulphite and methyl alcohol.

The equilibrium conditions in aqueous sulphur dioxide solutions are represented by the scheme:



The hydrogen sulphite ion, HSO_3' , is probably unstable and undergoes transformation into sulphurous acid and SO_3'' , thus: $2\text{HSO}_3' = \text{SO}_3'' + \text{H}_2\text{SO}_3$. The sulphurous acid then comes into equilibrium with sulphur dioxide hydrate in the sense $\text{H}_2\text{SO}_3 \rightleftharpoons \text{SO}_2 \dots \text{H}_2\text{O}$. These changes would explain the gradual development of the absorption band in hydrogen sulphite solutions. The view is expressed that the sulphite ion, $[\text{SO}_3]''$, has a symmetrical constitution, and hence also the normal sulphites. This view is supported by the observation that selenious acid and the dialkyl selenites have similar absorption spectra to the normal sulphites (compare A., 1917, ii, 61, 186; 1915, ii, 389). E. H. R.

The Ethylene Chromophore. H. LEY (*Ber.*, 1918, 51, 1808—1819. Compare Ley, A., 1917, i, 261; Kauffmann, *ebenda*, 391).—The absorption spectra of styrene, stilbene, and cinnamic acid and their derivatives have been studied. Bathochromic effects are produced by the introduction of a methyl, methoxy- or ethoxy-group in the ω -position in styrene, whilst a hypsochromic effect results when the methyl or ethoxy-group is substituted in the α -position; hypsochromic effects are also observed with 7-methylstilbene, β -methylcinnamic acid, β -ethoxycinnamic acid, and α -methylcinnamic acid as compared with the parent substances.

Attempts are also made to connect absorptiometric anomalies with abnormal values for the molecular refraction. The esters of α - and β -methylcinnamic acid are less absorbent than the parent substance and have lower values for the exaltation $\Sigma\alpha$. β -Methylstyrene has an absorption similar to that of styrene, and its refraction anomaly is of the same order. With the hydroxy-derivatives a somewhat similar parallelism is observed, the hypsochromic effect of the ethoxy-group in the α -position corresponding with a distinct diminution of the exaltation. Since, in general, an increase in refractive and dispersive power corresponds with an increase in the unsaturated nature of the compound, the explanation of the "disturbing" action of substituents on the absorption spectra of substances by the assumption of alteration in the degree of unsaturation appears to receive further support.

The extinction-coefficients of chloroform solutions of 1:3:5-trinitrobenzene and styrene, α -ethoxystyrene, β -ethoxystyrene, and β -methoxystyrene respectively have also been measured, but the results scarcely lead to a definite conclusion.

Kauffmann's criticism of the author's views (*loc. cit.*) is reviewed.

H. W.

Crystalloluminescence. II. Triboluminescence and Crystalloluminescence. HARRY B. WEISER (*J. Physical Chem.*, 1918, 22, 576—595. Compare A., 1918, ii, 419).—For the further investigation of the relationship between crystalloluminescence and triboluminescence, the phenomena have been studied with crystals of arsenic trioxide and the double sodium-potassium sulphate, $2\text{K}_2\text{SO}_4 \cdot \text{Na}_2\text{SO}_4$. In each case the colour of the light emitted by the crystals during rapid formation (crystalloluminescence) and that

produced by rubbing or crushing the crystals (triboluminescence) have been determined by photographing through an appropriate series of light filters, and it is shown that the light rays resulting from the two phenomena are identical in colour, that from arsenic trioxide differing considerably, however, from that from the double salt. The colour of the luminescence is therefore a specific property of the compound. The phenomena are held to be chemical in origin. Crystalloluminescence, which is only exhibited by a few inorganic compounds, is due to the rapid re-formation of molecules broken up by the process of electrolytic dissociation. Triboluminescence is due to the re-formation of molecules broken up by the violent disruption of crystals. Whilst all crystalloluminescent substances are also triboluminescent, the reverse is not true. In certain newly-formed crystals a state of strain may exist, and if outside force is applied to such crystals before the internal forces have become adjusted, violent disruption of the crystal may ensue, with consequent molecular decomposition and triboluminescence. The intensity of the triboluminescence depends on the force needed to break up the molecule and the magnitude of the conversion factor for light in the luminescent reaction.

E. H. R.

Spectrum of the Ruby and Emera'd. IV. Spectrum Phenomena in the Chromium Compounds. JAMES MOIR (*Trans. Roy. Soc. S. Africa*, 1918, 7, 129—130).—It has been shown previously (*ibid.*, 2, 321; 3, 271, 273; 4, 339) that the almost unique spectra of ruby and emerald are due to chromium oxide which has been compelled to vibrate in an abnormal or constrained manner leading to the production of narrow absorption bands; the constraining substance in the case of the ruby is crystalline alumina and in the case of the emerald it is glucinum silicate. The present communication describes attempts to induce the constrained vibration of ordinary chromium oxide by artificial means. Suitable methods consist in dissolving chromic oxide in concentrated sulphuric acid and gradually adding an organic substance, such as starch, until the orange colour has changed to deep green or, more strikingly, by replacing the sulphuric acid by glacial phosphoric acid. It would appear possible to get a very close imitation of the emerald spectrum by the latter process, but the ruby spectrum, on the other hand, has not been reproduced except by means of alumina.

Concentrated hydrochloric, nitric, perchloric, formic, acetic, and citric acids did not yield very characteristic results, although a faint, hazy band at λ 6800 was seen in several of these solutions. H. W.

A New Electrometer for the Measurement of Radioactivity. B. SZILARD (*Anal. Fis. Quim.*, 1918, 16, 690—699).—A detailed description of a new improved electrometer of the attracted aluminium needle type especially adapted for radioactive measurements.

W. S. M.

Radioactivity of some Canadian Mineral Springs. J. SATTERLY and R. T. ELWORTHY (*Trans. Roy. Soc. Canada*, 1917—1918, [iii], 11, 17—26).—The water of some sixty mineral

springs has been examined with respect to its content of radium emanation and dissolved radium. Measurements of the rate of flow and temperature of the water are also given, together with the nature of the strata. The emanation content varies from 11.2×10^{-12} curies per litre to 345×10^{-12} curies. The dissolved radium varies between the merest trace and 46×10^{-12} gram per litre, although in most cases the amount is very small. A tabular comparison is given between the factors for these springs and those of American and European springs. Thermal springs are shown to be more active than the cold springs. J. F. S.

The Radioactivity of Mud from Rockanje. E. H. BÜCHNER (*Chem. Weekblad*, 1918, 15, 243—246).—Examinations of samples of mud from the Waal lake, near Rockanje (A., 1913, ii, 821), showed proportions of radium of the order of 1×10^{-10} parts by weight. Subsequent examination in the following year confirmed this figure. More recent work on samples of the same material by Folmer and Blaauw (A., 1918, ii, 145) indicate a radium content of the order generally found in common rocks and deposits, namely, 1×10^{-12} . The author has examined some of the samples tested by Folmer and Blaauw, and confirms their results. The discordance between the later figures and the earlier results cannot be attributed to differences in the methods of working or to experimental error, but is possibly due to deposition from the river water in isolated places of matter containing a high proportion of some uranium mineral or its degradation products. S. I. L.

The Radioactivity of the Mud from Rockanje. A. H. BLAAUW (*Chem. Weekblad*, 1918, 15, 361—364).—Büchner's arguments (preceding abstract) to account for the differences shown by the later analyses in the radioactivity of the Rockanje deposits are criticised, and the assumptions of patches of higher activity questioned. Other geological arguments suggested by Büchner are shown to be incorrect. It is claimed that the later examination was complete. S. I. L.

Ionisation and Resonance Potential for Electrons in Vapours of Magnesium and Thallium. PAUL D. FOOTE and FRED L. MOHLER (*Phil. Mag.*, 1919, [vi], 37, 33—50).—The ionisation and resonance potentials for electrons in vapours of magnesium and thallium have been measured by the Tate modification of the Franck and Hertz method. The experimental values for magnesium vapour were 2.65 volts and 7.75 volts for the resonance and ionisation potentials respectively. The values calculated from the quantum relation $h\nu = eV$ are 2.70 volts and 7.61 volts respectively. In the case of thallium vapour, the values 1.07 volts and 7.3 volts were obtained for the resonance and ionisation potentials respectively. The theoretical value for the former quantity is 1.07 volts, whilst that of the latter is unknown. The ionisation potential for magnesium is obtained from the limit of

the combination series $1.5S - mp_2$, and the resonance potential is determined by the first line in this series, $m=2$. In the case of thallium, the resonance potential is determined by the shorter wave-length member of the first term of the principal series of doublets. No known series in thallium has a convergence frequency greater than 49,263. The observed ionisation potential for thallium suggests the presence of an undiscovered series of single lines converging at $\nu=1.5S=57,000$ to 60,000. The present work offers evidence that the single line spectra of magnesium and thallium are $\lambda=4571$ and $11,513$ Å. respectively. The general behaviour of the metals as regards ionisation and resonance potentials appears to be identical for metals in the same group of the periodic table. In the case of thallium, the component of the doublet having the higher frequency determines the value of the energy quantum absorbed by the atom. This fact suggests either the possibility of separate excitation of the components of a doublet by electronic impact or a behaviour of thallium vapour, thus excited, analogous to the emission of characteristic X-rays, for which the K group does not appear until the energy of the impacting electrons is greater than that corresponding with K γ . The authors have obtained a value of Planck's constant, h , by the method of ionisation and resonance potentials. Using thirteen determinations on seven different metals, the final mean value $h=6.55 \times 10^{-27}$ erg. sec. was obtained, which is in excellent agreement with recent determinations by other methods. The question of photoelectric sensibility of metallic vapours has been briefly discussed, and recent work on ionisation and resonance potentials has been considered critically.

J. F. S.

The Emission of Positive Electricity by Salts of the Alkalies and Alkaline Earths under the Influence of Canal Rays.

W. VÖLKER (*Ann. Physik*, 1918, [iv], 57, 257—277).—It is shown that when a suitably prepared thin layer of lithium chloride or of calcium sulphate, connected with a conducting system, is subjected to bombardment by canal rays, the induced currents can only be explained on the assumption that, when the cathode fall of potential exceeds a certain limiting value, positive charges are emitted by the salt. The limiting value of the cathode fall in the case of lithium chloride is about 500 volts, and with calcium sulphate about 1500 volts. These values correspond with the limiting values found by Stark and Wendt (A., 1912, ii, 720), above which these salts, under the influence of canal rays, emit the characteristic metallic series lines. It is concluded that the carriers which emit the series lines, which are only observed in the space immediately adjacent to the salt, are the positive ions of the metallic elements themselves.

E. H. R.

Measurement of Concentration of Hydrogen Ions and a New Form of Calomel Electrode. W. STURM (*Chem. Weekblad*, 1918, 15, 912—916).—The author has designed a

hydrogen electrode which reaches equilibrium in about five minutes. This consists of a flask fitted with a rubber stopper pierced with three holes. The electrode, which passes through one of the holes, consists of a glass tube open at its lower end, and is surrounded by a cylinder of platinum gauze. An inner tube carries a copper wire connected to the platinum gauze by means of mercury, and a platinum wire. Hydrogen enters through a tube in the second hole, passes up the electrode, and escapes through a side-tube. The third opening carries a thermometer. The arrangement has the advantage that the fluid is throughout agitated in contact with the hydrogen, which results in a rapid equilibrium. The disadvantage, however, is that a considerable volume of fluid is required. Oxygen is removed from the hydrogen by means of heated platinised asbestos; the presence of small quantities of oxygen must be studiously avoided.

A form of calomel electrode is described in which mercury, mercury-calomel paste, potassium chloride crystals, and saturated potassium chloride solution are employed; such an apparatus has been in use for eight months satisfactorily. S. I. L.

Electrolytic Conductivity in Non-aqueous Solutions. II. Electrical Conductivity of *p*-Tolyltrimethylammonium Iodide in Water and several Organic Solvents. HENRY

JERMAIN MAUDE CREIGHTON and D. HERBERT WAY (*J. Franklin Inst.*, 1918, **186**, 675—698. Compare *ibid.*, 1916, **182**, 745).—The electrical conductivity of *p*-tolyltrimethylammonium iodide has been determined at 25° in water, methyl alcohol, ethyl alcohol, propaldehyde, anisaldehyde, benzaldehyde, acetone, formic acid, acetic acid, propionitrile, benzonitrile, nitromethane, nitrobenzene, and *epichlorohydrin*. In the case of some of the solvents, measurements have also been made at 0° and 18° and the temperature coefficient calculated. *p*-Tolyltrimethylammonium iodide, like most strong electrolytes, does not follow Ostwald's dilution law in aqueous solution, but is approximately in agreement with the Storch empirical dilution equation. The ionic conductivity of the *p*-tolyltrimethylammonium ion at 25° in aqueous solution is 40.3. The equivalent conductivity at infinite dilution has been extrapolated for *p*-tolyltrimethylammonium iodide in all the solvents used, and it is shown that the values vary from $\Delta_{\infty} = 13$ in anisaldehyde to $\Delta_{\infty} = 188$ in acetone. Further, the magnitude of this value bears a relationship to the chemical constitution of the solvent, which may be generally stated thus: the equivalent conductivity of an electrolyte at infinite dilution, and consequently the velocity of the ions, is greater in an aliphatic solvent than in an aromatic solvent of corresponding constitution. Thus Δ_{∞} for nitromethane = 115, for nitrobenzene 38; for propionitrile 143, whilst for benzonitrile $\Delta_{\infty} = 54$. In an homologous series, the value for Δ_{∞} is greater the nearer the solvent stands to the beginning of the series. For example, Δ_{∞} for water = 116, methyl alcohol 100, ethyl alcohol 48, formic acid 90, acetic acid 25. Of

the various substituting groups, the influence of the aldehyde group on the magnitude of Δ_{∞} is greatest, whilst that of the carboxyl group is the least, as is shown by the series: acetaldehyde $\Delta_{\infty} = 188$, nitromethane 115, methyl alcohol 100, acetic acid 25.

J. F. S.

Electrolytic Deposition of Iron from Organic Solvents.

E. H. ARCHIBALD and L. A. PIGUET (*Trans. Roy. Soc. Canada*, 1917—1918, [iii], **11**, 107—112).—Solutions of ferric chloride in acetone, ethyl alcohol and acetone, and water and acetone, have been electrolysed by various currents and at various voltages at 25°. The experiments were carried out between platinum electrodes, but in some experiments a silver cathode was employed. In all cases, the iron can be completely deposited; in the case of acetone and of acetone-water mixtures, the iron is deposited free from carbon. At low voltages, the iron is deposited in the metallic condition; as the voltage is increased, it comes down as a red deposit which is adherent and allows the iron to be removed from the solution. From the acetone-alcohol solutions, the iron, although completely deposited, is contaminated with carbon. From acetone-water solutions of ferrous sulphate, the iron can be completely deposited, but the deposit contains a considerable amount of carbon. Aldehyde is not formed during the electrolysis of any of the solutions.

J. F. S.

Electrolytic Precipitation of Zinc. D. McINTOSH (*Trans. Roy. Soc. Canada*, 1917—18, [iii], **11**, 113—119).—The electrolytic deposition of zinc from solutions of the sulphate has been studied under various conditions with the object of ascertaining the most suitable conditions for obtaining good deposits. It is shown that the best results are obtained when the solution is free from colloids and when the amount of iron present is low. The metals arsenic, antimony, copper, cobalt, nickel, and all metals more electropositive than zinc must be absent. The solution, particularly in tanks containing large amounts of acid, should be cold. The zinc deposits in a semi-passive form; but when it begins to dissolve, solution cannot be stopped in any simple way. The zinc concentration should be as high as possible (6—7%), and no attempt should be made to electrolyse solutions containing less than 1.5—2.0% of zinc. With the ordinary cascade system the maximum current density is 25—30 amperes per sq. foot. A large number of photographs of deposits obtained under varying conditions are reproduced in the paper.

J. F. S.

Critical Phenomena. WILLIAM R. FIELDING (*Chem. News*, 1918, **117**, 379—383).—The relation between the critical pressure and critical temperature of an element can be expressed by the formula $(T_c + 236.2)/\sqrt{P_c} = 70.9$. This relation holds strictly for hydrogen and the members of the halogen group and less closely for nitrogen and xenon, whilst in the case of oxygen the divergence is considerable. For series of inorganic compounds such as that of the

halogen acids a similar formula holds, $(T_c - x) / \sqrt{P_c} = k$, where x and k are constants for any particular series. In inorganic compounds the critical pressure rises with the critical temperature in any series, but in organic compounds the pressure falls as the temperature rises. For a number of organic compounds the value of $T_c \times \sqrt{P_c}$ has been calculated. In higher members of aliphatic series this quantity tends to become constant. In the aromatic series of hydrocarbons, with the introduction of alkyl groups into the benzene ring, it first decreases, and as the complexity of the alkyl groups increases it becomes practically constant. Multiplication of benzene rings in the molecule produces a considerable increase in the value of the quantity.

E. H. R.

Calorimetric Lag. WALTER P. WHITE (*J. Amer. Chem. Soc.*, 1918, **40**, 1858—1872).—Lags may pertain to the thermometer, to various portions of the calorimeter, or to outlying bodies, including air. In this paper the lag of external bodies, such as a thin metal shield surrounding the calorimeter, is treated in a mathematical manner. The effects prove to be three: one, equivalent to a change in the heat capacity of the calorimeter, which can be eliminated by direct calibration of the calorimeter; another, much smaller, depending on the amount of thermal leakage, which can be avoided by using the adiabatic method; and a third, dependent on the jacket temperature, which disappears if this is constant.

On account of the lag effect, the effective heat capacity of a shield midway between calorimeter and jacket is only one-fourth its actual capacity, and, with due regard to the possibility of change, such shields may often be used to reduce thermal leakage. Used as a cover such a shield has a specially small error, and offers a particularly easy method of dealing with evaporation. (Compare A., 1918, ii, 149.)

E. H. R.

The Conditions of Calorimetric Precision. WALTER P. WHITE (*J. Amer. Chem. Soc.*, 1918, **40**, 1872—1886).—In a calibrated calorimeter most of the errors arise in thermometric measurements, and most of these come in the "cooling correction," the determination of the effect of thermal leakage. The leakage effect is equal to $K\phi_x T$, where T is the time, ϕ_x is the difference between calorimeter and environment temperature, and K the leakage modulus of the calorimeter. By diminishing K , as by means of a vacuum, the effect of errors in ϕ_x is diminished. These errors arise from the difficulty in getting the jacket and calorimeter temperatures uniform. The advantage of diminishing ϕ_x , the thermal head, is largely illusory, since the main error, that in determining K by means of the cooling rate, is little affected. Lags, which vary with K and are independent of T and ϕ , can be made to cause little or no error. The rate of stirring should be as uniform as possible, since the heat produced varies as the cube of the speed. The type of stirrer and design of the calorimeter with reference to stirring may be important.

E. H. R.

Calorimetric Methods and Devices. WALTER P. WHITE (*J. Amer. Chem. Soc.*, 1918, **40**, 1887—1898).—The general rules for calorimetric precision (preceding abstract) are applied to jacket covers and stirrers and to such special devices as vacuum-jacketed vessels, the adiabatic method, aneroid or dry calorimeters, double or differential calorimeters, and measured-shield calorimeters, and the advantages of the different forms of calorimeter are compared. The measured-shield calorimeter is a new device, having between the calorimeter and the jacket a thin metal shield connected to the wall of the jacket by thermo-elements which are used to measure the thermal head. E. H. R.

Sensitive Bath Thermostat. A. NORMAN SHAW (*Trans. Roy. Soc. Canada*, 1917—18, [iii], **11**, 129—135).—A thermostat on a rather large scale is described which differs but little from the well-known types. A note on the regulation of temperature is appended to the paper. J. F. S.

An Accurate Method for Measuring the Density of Gases. O. MAASS and J. RUSSELL (*J. Amer. Chem. Soc.*, 1918, **40**, 1847—1852).—The method described is applicable to the determination of the density of those gases which can be condensed by liquid air or some other freezing agent. The purified, dry gas is condensed in a suitable vessel, and thence transferred to a large exhausted glass flask (about $2\frac{1}{4}$ litres capacity) the volume of which is accurately known. The flask has a connection to a manometer, and the pressure is read at 0° , the flask being immersed in ice. By a suitable arrangement of tubes the gas in the flask can be transferred to an exhausted glass bulb immersed in liquid air. When the gas has liquefied, the bulb is sealed off and weighed, and again weighed after it has been opened and the liquid allowed to evaporate. The pressure of the gas remaining in the flask and connecting tubes is read after the bulb has been detached, to enable the volume of gas taken into the bulb to be calculated. The accuracy of the method is limited by the accuracy with which the height of the mercury in the manometer can be read. The probable error with the method used is 0.05%; with the aid of a cathetometer it could be reduced to 0.01%.

The following densities were determined: acetylene, 1.1695; methyl ether, 2.1103; hydrogen bromide, 3.6397. E. H. R.

The Change of Density of Liquid Mixtures with Increasing Temperature. W. HERZ (*Zeitsch. anorg. Chem.*, 1918, **104**, 251—252).—The formula expressing the relationship between density and temperature, $1/d_t = a - b \log(\theta - t)$, where d_t is the density at temperature t , θ is the critical temperature, and a and b are constants, has been found to hold for liquid mixtures as well as for pure liquids. Different binary mixtures of benzene, toluene, aniline, and nitrobenzene were used for the experiments, at temperatures between 25° and 90° , and the differences between observed and calculated densities were very small.

The critical temperature θ of the mixture was calculated from those of the constituents, θ_1 and θ_2 , by means of the formula $\theta = n\theta_1 + (100 - n)\theta_2/100$, where n and $(100 - n)$ are the percentages of each constituent.

E. H. R.

Molecular Attraction and Attraction of Mass, and some New Gas Equations. JAMES KAM (*Phil. Mag.*, 1919, [vi], 37, 65—97).—A theoretical paper, in which gas equations are deduced from considerations of the actual and theoretical co-volumes. A general equation is deduced which considers the effect of temperature on the relation of the co-volumes to the volume. Further reduced isothermals and reduced border-curves are considered. It is shown that the cohesive forces causing the "inward pressure" appear to follow a law similar to the inverse square law of mass attraction. From the deviations from the gas laws a value for the tensile strength of iron is deduced which is of the same order as the experimental value. It is further shown that whatever the ultimate nature of the cohesive forces may be, they seem to be proportional to the square of the molecular weight and to obey the inverse square law—a law consequently similar to Newton's law of attraction of mass.

J. F. S.

Internal Molecular Forces of Solid Substances and their Relations with the Elastic Properties. STEFANO PAGLIANI (*Nuovo Cim.*, 1918, [vi], 15, i, 103—129).—The existence of three forms of internal molecular forces in solids is considered and their values calculated. The first, F , termed intermolecular force of coherence, enters as a factor in the internal work into which thermal or mechanical energy can be transformed without change in the volume of the substance. The second, π , termed internal pressure, is analogous in character to external pressure, and enters as a factor in the internal work in which thermal energy is used with variation of the volume of the substance. The third, called intermolecular force of change of phase, enters as a factor in the internal work accomplished during changes of phase—in the fusion of solids; this force, which acts at the temperature of fusion, where Lindemann considers that the amplitudes of the atomic oscillations about their equilibrium position become of the same order of magnitude as the mean distance between the atoms, appears to be of the same nature as F , which acts with definite values at different temperatures.

The magnitude of the force F exhibits relationships with the values of some of the magnitudes considered in the study and applications of the elastic properties of solids. The simplest of these relations with the moduli of elasticity of tension E , of rigidity n , and of flow N are as follows: $E = 1.70 F$ or approximately $E = 5F/3$, $n = F/\pi$, and $N = 2F/\pi$. The relatively great value of the ratio between E and F depends on the fact that the load E , which should double the initial length of the solid, is only an ideal load unattainable in practice. It is hence more accurate to replace E in technical formulæ by F , this being a real magnitude the value

of which at different temperatures may be calculated by means of physical magnitudes exactly measurable; a number of expressions are given in which this substitution is made. The modulus of elasticity for each species of deformation is found to be directly proportional to the molecular force of coherence. T. H. P.

The Adsorption of Arsenious Acid by Ferric Hydroxide.

MAITLAND C. BOSWELL and J. V. DICKSON (*J. Amer. Chem. Soc.*, 1918, **40**, 1793—1801).—The adsorption of arsenious acid from solution, by ferric hydroxide which had been prepared several months previously, has been studied both in presence and absence of sodium hydroxide. The adsorption of the arsenious acid by the ferric hydroxide is diminished by the presence of sodium hydroxide, whilst the adsorption of the sodium hydroxide is itself increased by the presence of the arsenious acid. The age of the ferric hydroxide and the addition of sodium chloride appear not to have any effect on the quantitative data recorded.

The results follow only approximately the "adsorption law," $E = \beta A^p$, where E is the concentration of the adsorbed substance in the adsorbing phase, A its concentration in the solution at equilibrium, and β and p are constants. The equation can be written $\log E = p \log A + B$. Hence if the logarithms of the concentrations in the adsorbent and the solution be plotted, a straight line should be obtained, the slope of which gives the value of p whilst the intercept gives the value of $B = \log \beta$. The curves thus obtained from the results of the authors' experiments approximate to straight lines, but all show a distinct concavity to the x or $\log A$ axis. The adsorption phenomenon cannot be exactly represented by the above equation. The adsorption of arsenious acid by ferric hydroxide was also studied by Mecklenburg (A., 1913, ii, 676), who concluded that the adsorption curves for any particular gel prepared under varying conditions are so related to a unit curve that the ratio of any ordinate on one curve to the corresponding ordinate on the unit curve is a constant. The authors interpret this to mean that the exponent p in the equation $E = \beta A^p$ is constant for any particular gel, whilst β is a variable depending on the conditions of preparation of the gel. The values of p calculated from the authors' and Mecklenburg's results agree when arsenious acid is used alone, but in presence of sodium hydroxide its value increases. E. H. R.

Ferment Action. II. Adsorption of Amino-acids and Polypeptides by Animal Charcoal. Relation of the Observed Appearances to the Cleavage of Polypeptides by Yeast Juice.

EMIL ABDERHALDEN and ANDOR FODOR (*Fermentforsch.*, 1917, **2**, 74—102; from *Chem. Zentr.*, 1918, ii, 738. Compare A., 1917, i, 306).—Animal charcoal adsorbs scarcely a trace of glycine, but it adsorbs a little alanine and a comparatively large quantity of leucine. Similar variations are observed in the case of the polypeptides, even isomeric substances being adsorbed to very different extents by the charcoal. The amount adsorbed at various dilutions

varies according to the laws of adsorption, just as has been observed in the case of enzymes. The adsorptive power of charcoal differs from that of the enzymes, however, in being uninfluenced by changes in the concentration of the hydrogen and hydroxyl ions in the solution.

When mixtures of amino-acids or polypeptides are treated with animal charcoal, the adsorption of the substances containing the more complex molecules is relatively increased, whilst that of smaller molecular substances is decreased. H. W. B.

Ferment Action. III. Adsorption of Amino-acids and Polypeptides and also of various Carbohydrates by Animal Charcoal. EMIL ABDERHALDEN and ANDOR FODOR (*Fermentforsch.*, 1917, **2**, 151—166; from *Chem. Zentr.*, 1918, ii, 739. Compare preceding abstract).—*L*-Arabinose, lævulose, and inositol are less readily adsorbed by charcoal than dextrose, sucrose, and other disaccharides and trisaccharides. The presence of carbohydrates diminishes the adsorptive power of animal charcoal towards polypeptides, and conversely the adsorption of carbohydrates is adversely influenced by polypeptides. H. W. B.

Retardation by Sugars of Diffusion of Acids in Gels. EVARTS A. GRAHAM and HELEN TREDWAY GRAHAM (*J. Amer. Chem. Soc.*, 1918, **40**, 1900—1917).—The rates of diffusion of a number of inorganic and organic acids into gelatin solutions containing varying amounts of dextrose, sucrose, and lactose have been measured. All the sugars have a marked retarding influence on the diffusion of any acid, the disaccharides having a considerably greater effect than the monosaccharide. In agreement with the general diffusion law, the ratio of the distance of diffusion to the square root of the time is found to be a constant in gelatin both with and without sugar. The retardation is not proportional to the concentration of the sugar, but is relatively greater for smaller concentrations of sugar. If the ratio d/\sqrt{t} is equal to K_0 without sugar and K with sugar, the relative retardation is given by $(K_0 - K)/K_0$ or Δ/K_0 . The relation between concentration of sugar and retardation can be expressed approximately by the equation $(\Delta/K_0)^n = ac$, where c is the concentration and a and n are constants. In 10% gelatin, nitric acid behaves abnormally in that the ratio d/\sqrt{t} is not constant, but increases rapidly at first and, after remaining constant for some time, again decreases. Hydrochloric acid shows the same behaviour in 3% gelatin.

Sodium chloride also retards the diffusion of acids into gelatin, but to a less extent than the sugars when equimolecular solutions are compared. This is the reverse of their effect in reducing the acid swelling of gelatin, in which sodium chloride is more effective than sugar. The physiological bearing of the results obtained is briefly discussed, particularly with reference to the protective action of dextrose in cases of chloroform poisoning, the effects of

which are ascribed to the presence of free hydrochloric acid in the substance. The mechanism of the retardation is also discussed.

E. H. R.

Chemical Affinity in Crystals and the Velocity of Crystallisation. M. PADOA (*Atti R. Accad. Lincei*, 1918, [v], 27, ii, 59—64; *Gazzetta*, 1918, 48, ii, 139—147).—The suggestion is made that, in most cases, crystallisation represents a transposition effected by means of valencies among the more or less free molecules of the gaseous or liquid phase, so that velocity of crystallisation may be regarded as velocity of reaction. The author has measured the velocities of crystallisation of a number of super-cooled compounds with the object of ascertaining: (1) if, with isomorphous compounds of similar structure, the velocities of crystallisation are equal or of the same order of magnitude, and (2) if, in a series of compounds of perfectly analogous chemical constitutions, the velocities of crystallisation are comparable and, *ceteris paribus*, dependent on the molecular weights. Similar values are obtained for *m*-bromo- (600) and *m*-chloro-nitrobenzene (882), and also for *p*-dichloro- (4800), *p*-dibromo- (7000), and *p*-iodo-benzene (6000), the low value for *p*-chloriodobenzene (1153) being apparently dependent on its markedly different viscosity. The introduction of methyl into the benzene ring greatly retards the crystallisation; naphthalene and its analogues show far lower values than benzene, the isomeric anthracene and phenanthrene having identical velocities. Similarity also exists between the velocities for isomorphous inorganic compounds.

Of two compounds of similar structure, the one saturated and the other unsaturated, the latter should present the greater velocity of crystallisation, since the latent affinities in the double linkings should favour the process of crystallisation. This conclusion is completely confirmed by the results obtained for a number of pairs of isomorphous organic compounds, one member of each pair being saturated or at least less unsaturated than the other member.

The general conclusions drawn are: (1) the velocity of crystallisation is a constitutive property, and (2) the bonds between the atoms in crystalline networks are of the same nature as chemical valencies.

T. H. P.

Point of Transformation between Reversible Modifications. C. VIOLA (*Atti R. Accad. Lincei*, 1918, [v], 27, ii, 107—112).—The author applies the law of maximum work and Curie's law to the consideration of the possible co-existence, at a temperature different from T , of two reversible crystalline modifications which occur in contact in stable equilibrium at temperature T and at a definite pressure. It is shown that, either where a process is effected reversibly and crystallisation takes place and should take place according to Curie's law, or where between two modifications in contact a minimal surface tension is established, a point of

transformation must always exist there; vice versa, the surface tension is a minimum at a transformation point between two modifications.

T. H. P.

The Artificial Coloration of Liquid Crystals. PAUL GAUBERT (*Compt. rend.*, 1918, **167**, 1073—1075).—Indophenol may be satisfactorily used for colouring liquid crystals and also solid crystals of a large number of organic compounds. The presence of the indophenol lowers the solidification point of the molten substances, and in the case of substances giving several birefringent liquid phases, all the melting points or transformation points are lowered. There exists for the indophenol a coefficient of solubility particular to each phase, this coefficient diminishing with the molecular volume.

The optically positive liquid crystals obtained by combining cholesterol with glycollic acid, glycerol, etc., are not coloured by indophenol, although the isotropic liquid dissolves it. W. G.

Theory of the Velocity of Coagulation. H. FREUNDLICH (*Kolloid Zeitsch.*, 1918, **23**, 163—173).—A theoretical paper in which it is shown that the velocity of slow coagulation of hydrophobe sols increases very much with increasing concentration of the coagulating electrolyte, whilst for rapidly coagulating sols the velocity of coagulation is constant and independent of the nature and concentration of the electrolyte. Smoluchowski explains the rapid coagulation by assuming that the collisions between the particles are non-elastic and lead to the coagulation of all the particles which come within the sphere of influence. The rapid increase in velocity of the slow coagulation is explained by the assumption that in the concentration present the charges on the particles produce a repulsion, and only those particles are coagulated the kinetic energy of which is greater than a certain critical value. This critical value is greater the greater the charge on the particle. The number of these particles increases as the electrolyte concentration increases. A formula giving the relationship between electrolyte concentration and velocity of coagulation is given, and this is in keeping with observed results. J. F. S.

The Brownian Movement and the Coagulation of Colloidal Solutions. H. W. WOUDESTRA (*Chem. Weekblad*, 1918, **15**, 679—680).—The author claims priority over Kruyt and van der Spek (*A.*, 1917, ii, 563) in directing attention to the function of the Brownian movement of the colloid particles in the coagulation of a colloidal solution. W. S. M.

The Brownian Movement in Relation to the Mechanism of Flocculation. D. J. HISSINK (*Chem. Weekblad*, 1919, **16**, 20—21).—The author disputes the contention of Henri and Ostwald (see "Grundriss der allgemeinen Chemie," 1917, 544) that the Brownian movements are diminished by addition of a coagu-

lating electrolyte before coagulation, and contends that by microscopic observation it can easily be seen that the coagulation itself is the cause of the diminution of the movement, which is therefore a consequence of the coagulation and does not precede it.

S. I. L.

The Lowering of the Degree of Dissociation. R. N. DE HAAS (*Chem. Weekblad*, 1918, **15**, 1352—1355).—An elementary mathematical consideration of the fundamental equation of mass action with reference to the shifting of the equilibrium consequent on the addition of one of the products of dissociation or ionisation to the system.

W. S. M.

Heterogeneous Equilibria between Aqueous and Metallic Solutions: The Interaction of Mixed Salt Solutions and Liquid Amalgams. V. A Study of the Ionisation Relations of Potassium and Strontium Chlorides in Mixtures. G. MCP. SMITH and EDWIN ARTHUR REES (*J. Amer. Chem. Soc.*, 1918, **40**, 1802—1847).—To study the equilibrium between mixed strontium and potassium amalgams and the mixed aqueous solutions of the chlorides of these metals, a definite quantity of either strontium amalgam or potassium amalgam of known concentration was shaken up with successive portions of a known aqueous solution of the mixed chlorides until equilibrium was reached. The quantities of strontium and potassium in the amalgam were then determined by analysis. Experiments were made on the effect of varying (1) the amalgam concentration up to about 0.6 milli-equivalent of potassium or strontium per 10 grams of mercury, (2) the total salt concentration in the aqueous phase from 0.05*N* to 3*N*, (3) the ratio of the two salts in the aqueous phase at different total salt concentrations, and (4) the temperature from 15° to 40°. To interpret the data obtained, the value of the expression $(\text{Sr}_{\text{Hg}})(\text{K-salt})^2/(\text{K}_{\text{Hg}})^2(\text{Sr-salt}) = C_c$ was calculated, in which (Sr_{Hg}) and (K_{Hg}) are the respective atom-fractions in the mercurial phase, and (K-salt) and (Sr-salt) are the mol-fractions in the aqueous phase (compare A., 1917, ii, 247). The value of the "equilibrium expression" C_c increases proportionately with the total concentration in the mercurial phase up to 0.3 milli-equivalent per 10 grams of mercury, at temperatures from 15—45°. When the amalgam concentration is kept constant and the concentration of the aqueous phase increased, the proportions of the two salts being kept constant, the value of C_c first falls rapidly as the concentration rises to about 0.4*N*, but with stronger solutions it approaches a constant value.

Assuming that, in the most dilute solutions examined, 0.05*N*, an equimolecular mixture of the two salts is completely ionised, it is shown that, as the concentration in the aqueous phase is increased, but the salt ratio kept constant, the proportion of K^+ ions to Sr^{++} ions increases rapidly; also when the ratio of

potassium chloride to strontium chloride is increased, the proportion of K^+ ions increases at a greater rate.

The results obtained at different temperatures have been used to calculate the heat of reaction accompanying the changes between 15° and 40° . With rising temperature, the reaction is exothermic, and the heat of reaction is found to decrease with increasing total salt concentration.

As regards the dissociation of potassium and strontium amalgams, it is shown that the ordinary mass-action expression holds good for mixtures of the two up to a total concentration of about 2 milli-equivalents per 100 grams of mercury. There is evidence of the formation in the aqueous salt mixture of molecular complexes and complex ions, the results being in harmony with Werner's views.

E. H. R.

Influence of Substitution of the Components of Binary Equilibria in Solution. XIII. The Solution Equilibria of the Three Isomeric Phenylenediamines with Phenols and the Dinitro-derivatives of Benzene respectively.

ROBERT KREMANN and WOLFGANG STROHSCHNEIDER (*Monatsh.*, 1918, **39**, 505—570. Compare this vol., ii, 15).—Melting-point and cooling curves have been obtained for the six binary systems made up of the three phenylenediamines with either α -naphthol or β -naphthol, for the four binary systems composed of α - or β -naphthol with α - or β -naphthylamine, for the system β -naphthol and *p*-toluidine, for the nine binary systems composed of one of the three diphenylamines with one of the three dihydroxybenzenes, for the three binary systems composed of 2:4-dinitrotoluene with each of the phenylenediamines, and for the nine binary systems composed of one of the three phenylenediamines with one of the dinitrobenzenes. The results are given in curves and in voluminous tables. It is shown that *p*-phenylenediamine forms compounds with two molecules of α -naphthol (m. p. 110°) and with two molecules of β -naphthol (m. p. 150.5°). One molecule of *m*-phenylenediamine forms compounds with two molecules of β -naphthol (m. p. 114°) and with one molecule of α -naphthol (m. p. 35°). One molecule of *o*-phenylenediamine forms compounds with one molecule of α -naphthol (m. p. 60°) and with one molecule of β -naphthol (m. p. 86°) respectively. α -Naphthol forms two compounds with α -naphthylamine with one and four molecules of the latter to one of the former compound. A compound is formed containing two molecules of β -naphthol to three molecules of α -naphthylamine, but no compounds are formed between α -naphthol and β -naphthylamine; a simple eutectic is produced by these substances at 47° , and contains 56.5% of the last-named component. An equimolecular compound is formed between β -naphthol and *p*-toluidine (m. p. 87.5°). Equimolecular compounds are formed with *m*-phenylenediamine and catechol (m. p. 64.5°), *m*-phenylenediamine and resorcinol (m. p. 79°). *m*-phenylenediamine and quinol (m. p. 127°), with two molecules of catechol and one mole-

cule of *p*-phenylenediamine, with three molecules of catechol and two molecules of *p*-phenylenediamine, and with three molecules of quinol with one molecule of *p*-phenylenediamine. The details of the system *o*-dinitrobenzene-*p*-phenylenediamine have not been worked out, because of a secondary chemical reaction which interferes with the measurements. Compounds are formed between *m*-dinitrobenzene and the three phenylenediamines of the following composition: (i) three molecules of the nitro-compound with two molecules of *o*-phenylenediamine, (ii) two molecules of the nitro-compound with one molecule of *o*-phenylenediamine, and (iii) one molecule of the nitro-compound with two molecules of *m*-phenylenediamine; no compounds are formed between *p*-phenylenediamine and *m*-dinitrobenzene. In the case of *p*-dinitrobenzene and the three phenylenediamines, compounds are not formed with *o*- and *m*-phenylenediamine, but with *p*-phenylenediamine, a compound of two molecules of the amine and one molecule of the nitro-compound is formed. Full details of the numerous eutectics are given in the paper. J. F. S.

The Dilution Limits of Inflammability of Gaseous Mixtures. III. The Lower Limits of some Mixed Inflammable Gases with Air. IV. The Upper Limits of some Gases, Singly and Mixed, in Air. HUBERT FRANK COWARD, CHARLES WILLIAM CARPENTER, and WILLIAM PAYMAN (T., 1919, 115, 27—36).

The Propagation of Flame through Tubes of Small Diameter. II. WILLIAM PAYMAN and RICHARD VERNON WHEELER (T., 1919, 115, 36—45).

The Inflammation of Mixtures of Ethane and Air in a Closed Vessel. The Effects of Turbulence. RICHARD VERNON WHEELER (T., 1919, 115, 81—94).

The Ignition of Explosive Gases by Electric Sparks. JOHN DAVID MORGAN (T., 1919, 115, 94—104).

The Range of Existence of Substances, Kinetic Analysis, and the Estimation of Vapour Pressures from Reaction Velocities. M. TRAUTZ (*Zeitsch. anorg. Chem.*, 1918, 104, 169—210).—The author distinguishes between the range of stability and the range of existence of any substance. The stability of a substance is dependent on the chemical factors which bring about its formation, and is measured by the energy of the reaction, whilst its range of existence is determined only by the heat of activation needed to bring about its decomposition. The upper limit of existence of a compound is determined by the heat of activation of that binary decomposition which requires the least energy.

From the point of view of the author's theory of reaction velocity (A., 1917, ii, 23; 1918, ii, 151), a large number of reactions are

discussed. The formation of nitrosyl chloride or of nitrosyl bromide is apparently a reaction of the third order, but in all probability is made up of superimposed reactions of lower orders, and formulæ are developed by means of which the higher order reaction can be expressed in terms of reactions of lower orders. On the assumption that nitrosyl chloride formation proceeds in the two stages $\text{NO} + \text{Cl}_2 = \text{NOCl}_2$, $\text{NOCl}_2 + \text{NO} = 2\text{NOCl}$, a method of kinetic analysis is developed which enables the concentration and heat of formation of the intermediate product to be calculated. The heat of formation of NOCl_2 is 2500 cal.

The reaction between hydrogen and oxygen in porcelain vessels was supposed by Bodenstein to be of the third order, but the velocity constants do not distinguish between a third- and a second-order reaction. Moreover, probable values for the impact constant are obtained only if it is treated as a second-order reaction. The course of the reaction is probably $\text{H}_2 + \text{O}_2 = \text{H}_2\text{O}_2$ (measurable); $\text{H}_2\text{O}_2 + \text{H}_2 = 2\text{H}_2\text{O}$ (immeasurably fast). The probable value of the heat of activation for $\text{H}_2 + \text{O}_2$ is 46,374 cal., and the mean diameter of oxygen and hydrogen molecules, 1.62×10^{-8} cm.

The formation of nickel carbonyl from nickel and carbon monoxide, which is apparently a third-order reaction, probably proceeds in the three stages: $\text{Ni} + \text{CO} = \text{NiCO}$ (momentary equilibrium), $\text{NiCO} + \text{CO} = \text{Ni}(\text{CO})_2$ (measurable), and $\text{Ni}(\text{CO})_2 + 2\text{CO} = \text{Ni}(\text{CO})_4$ (immeasurably fast). It is shown how, from the velocity of the reaction, the vapour pressure of nickel can be calculated, and also its probable boiling point, 3358° A.T. The true order of a reaction, for example, in the case of nickel carbonyl formation, can be determined by consideration of the absolute reaction velocity and its temperature coefficient when the mean molecular diameter is assumed.

The velocity of surface reactions is fully discussed, and in this connexion the decomposition of ammonia, phosphine, arsine, and antimony hydride are considered. These reactions are assumed to be of the first order, corresponding with $\text{XH}_3 \rightarrow \text{XH} + \text{H}_2$ (measurable). The heat of activation in this series decreases with increasing molecular weight. From the heat of activation, the maximum wave-length of the actinic rays which will bring about the decomposition is calculated from the formula

$$q_0 = (2.843 \times 10^7) / \lambda.$$

It is concluded that ammonia, phosphine, and arsine should show absorption in the ultra-violet, antimony hydride in the visible spectrum. For ammonia, the maximum wave-length is shown to be $219.6 \mu\mu$, and in confirmation of this, it is shown experimentally that light of $214\text{--}203 \mu\mu$ is photochemically active towards ammonia.

Other reactions discussed are the formation and decomposition of sulphuryl chloride, the decomposition of sulphur trioxide and hydrogen selenide, the formation of hydrogen sulphide and hydrogen selenide from their elements, and the slow combustion of hydrogen iodide, of phosphorus, sulphur, and carbon. From Rhead

and Wheeler's experiments on the combustion of carbon to carbon monoxide (T., 1912, 101, 846), assuming that the vapour of carbon is monatomic, the boiling point of carbon is calculated to be 3542° and its vapour pressure in mm. of mercury at 1100° , 4.05×10^{-9} , the corresponding concentration being 4.74×10^{-14} mols. per litre.

E. H. R.

Consecutive Reactions. IV. Relationships of the Constants in the Acid Hydrolysis of Esters of Oxalic and Malonic Acids. ANTON SKRABAL and (Frl.) DANICA MRAZEK (*Monatsh.*, 1918, 39, 495—503. Compare A., 1917, ii, 250).—The kinetics of the acid hydrolysis of methyl oxalate, ethyl oxalate, methyl malonate, and ethyl malonate have been studied at 25° . The hydrolysis was effected by 0.1*N*-hydrochloric acid, and since, as has been previously shown, the determination of the change in acidity did not yield a satisfactory constant, the amount of normal ester remaining unchanged was determined iodometrically. In this way, it is shown that the hydrolysis takes place according to the equations for first-order reactions. The ratio of the reaction constants of the two consecutive reactions is 2:1. Methyl oxalate is hydrolysed approximately twice as rapidly as ethyl oxalate, but in the case of the malonic esters, the rate of hydrolysis is approximately the same in the two cases.

J. F. S.

The Conception of the Chemical Element as Enlarged by the Study of Radioactive Change. FREDERICK SODDY (T., 1919, 115, 1—26).

Atomic Weights in 1917. E. MOLES (*Anal. Fis. Quim.*, 1918, 16, 625—653).—A review of the work on the determination of atomic weights published during 1917.

Complex Ions. I. M. KOLTHOFF (*Chem. Weekblad*, 1918, 15, 1636—1644).—The definitions of complex ions given by de Haas (*ibid.*, 1917, 14, 752; 1918, 15, 1352) and Abegg and Bodländer (A., 1899, ii, 542) are criticised. The latter state: "One of the ion-forming components of a complex compound is built up of a single ion with an electrically neutral molecule." de Haas in his later paper defines an inorganic complex ion as "a metal-containing ion built up of one or more molecules and one or more ions." The author does not regard the presence of a neutral molecule as essential. Complex ions arise from the tendency of ions to combine with other molecules or ions, which tendency is the greater the lower is the "electro-affinity" of the ion; the nature of the complex is dependent also on the properties of the molecules or other ions which enter into it. It follows that for any salt, formation of complex ions becomes important only when neutral molecules are present to enter into combination with the ions, that is, when the degree of dissociation is small. Thus salts of strongly electropositive and electronegative ions or groups, and salts of one

strong and one weak radicle, being highly dissociated in solution, show small tendency to complex formation; salts of one strong and one weak radicle or element may, however, form complex ions by combination of the ions of the weaker element or radicle with each other.

The mercuric salts afford numerous examples of the formation of complex ions; dissociation of mercuric chloride forms the ions HgCl^+ , Hg^{++} , and Cl^- , and combination of the Cl^- with the undissociated molecule gives rise to the complexes HgCl_3^+ and HgCl_4^{++} . Of these, the group HgCl^+ has the highest concentration, namely, about 10,000 times as great as the concentration of the Hg^{++} ion. A consideration of the possibilities of combination or dissociation of a group AB^+ , where A is a bivalent positive and B a univalent negative ionogen, will show that the neutral molecule AB_2 can be regarded as an intermediate product between the complexes AB^+ and AB_3^+ .

The cases of formation of complexes fall into two classes. In the first, the electro-affinity of both ions is great, and the tendency to complex formation small, increasing as the electro-affinity falls. In the case of the chlorides of the alkali metals in solution in presence of an alkaline earth chloride, for example, the lower dissociation of the alkaline earth chloride causes the presence of its neutral molecules, which form complexes with the chlorine ion of the alkali metal chloride, of the type RCl_3^+ ; in concentrated solutions, the product of the concentration of this complex and that of the ion of the alkali metal may be so great as to cause separation of double salts. In the second class, the electro-affinity of both ions is small; it is clear that there will be a gradual transition between the two classes. Silver iodide and mercuric cyanide form examples of slightly soluble salts in this class; here the solubility is greatly increased by presence of either ion, owing to the possibility of complex formation which this introduces. Cadmium iodide affords a good case of a soluble salt of this class.

Consideration is given to complex ions containing hydrogen. For the case of a weak dibasic acid, H_2A , two dissociation constants, corresponding with the ions HA^+ and A^{++} , have to be considered, the second being usually very small. It is shown that the low dissociation of HA^+ as compared, for example, with RA^+ , where R is an alkali metal, is in contrast with the case of the halogen acids and the alkali haloids, the former having here the higher dissociation.

The following definition is finally put forward: "Complex ions break up to a certain extent into simple ions, generally with formation of neutral molecules."
S. I. L.

The Valency-hypothesis of J. Stark. W. JACOBS (*Chem. Weekblad*, 1918, 15, 1566—1571).—The theory of partial valencies has been employed to explain molecular aggregation in the fluid and crystalline states and to account for the various states of aggregation in which elements and compounds exist at ordinary

temperatures, and the changes in the states of aggregation which they undergo with change of temperature. The lines of force of a valency-electron can be distributed partly to atoms of the same molecule and partly to other molecules; consequently, intramolecular linking and intermolecular linkings are essentially due to the same forces, and all substances fall within a series in which the relative strength of the two classes of linking gradually changes. If the valency-electron is adjacent to a positive surface within its own molecule, intermolecular attraction will be weak and will be easily overcome by a small inflow of energy from without, which will leave the intramolecular system unchanged; at the other extreme, the strength of the two kinds of linkings approaches equality, the molecule behaves, as it were, like a single atom, and intermolecular aggregation is pronounced. In the last case, any disturbance of the intermolecular linkings must affect strongly the internal arrangement of the single molecules, and it may happen that a particular atomic system can only exist within very narrow limits of physical properties.

Stark has directed attention to the distinction between the meaning of the term molecule in the chemical and in the physical sense; in the former, molecules are distinguished as having identical arrangements of atoms, in the latter as being particles free to move in space in a definite manner determined by thermal conditions. The two definitions agree for molecules in the gaseous condition, since here no intermolecular linkings exist. In the crystalline condition, a chemical molecule is not free to move independently of its neighbours, and the physical definition fails. In the liquid condition, molecular aggregation occurs, but generally varies continually in strength and character; physical molecules exist, but are generally not identical with chemical molecules, being usually built up of several chemical molecules and varying continually in mass. In the case of solution, the molecules of solute by the attraction of their partial valencies form "solution molecules" with molecules of the solvent, each of which is a free-moving physical molecule and changes readily with slight changes of temperature.

Where intramolecular attraction is weak and the electric valency-field is diffused outside the molecule, as in the case of metals and electrolytes, the power of crystallisation is high, and in the liquid condition the substance has low vapour pressure; where the intramolecular linkings are very strong, as with the inert gases, the substance cannot be liquefied or solidified at ordinary temperatures. The gradation of physical properties of the hydrocarbons similarly is explained by the gradual decrease of strength of the intramolecular bonds as the number of similarly linked atoms within the molecule increases.

S. I. L.

A Device for Introducing a Vapour into a Gas. E. H. ZEITFUCHS (*J. Amer. Chem. Soc.*, 1918, **40**, 1899).—To introduce a known quantity of vapour into a stream of gas, the following

device is used. On to the end of a burette is sealed a glass capillary. This capillary is enclosed by the constricted end of a wide tube, closed at the top just below the cock of the burette by a piece of rubber tubing, which keeps it in position. The capillary touches in the wide tube a roll of asbestos fibres, wound round with resistance wire, by which it is heated electrically. A measured quantity of liquid can be run from the burette on to the asbestos fibre, where it is vaporised and taken up by a stream of gas entering the constricted portion of the tube by a side-tube and passing down through the asbestos roll. Any known quantity of vapour can thus be introduced into the gas. E. H. R.

Stopcock for Dropping Liquids arranged for Equalising the Pressure Above and Below the Outlet in the Stopcock.

HARRY L. FISHER (*J. Ind. Eng. Chem.*, 1918, **10**, 1014—1015).—An annular groove is provided in the key of the stopcock and a central tube is fitted in the two arms. The groove is in connexion with the outer tube, so that, when the tap is turned off, there is still communication between the atmospheres in the vessels above and below the stopcock. The liquid flows from the upper to the lower vessel through the central tube and the bore of the stopcock. W. P. S.

Inorganic Chemistry.

Recovery of Perchlorate Residues from Potassium Estimations. A. VÜRTHEIM (*Chem. Weekblad*, 1918, 15, 581—584. Compare A., 1917, ii, 568).—The usual method for the recovery of perchloric acids is to transform all the reagent into its potassium salt, which is easily purified by recrystallisation, and to distil the mixture of this salt with an excess of sulphuric acid in a vacuum. This method allows of recovery of only 25% of the quantity of acid originally used, and, moreover, requires a good vacuum pump. A method has now been devised which consists of the addition of unslaked lime to the collected alcoholic filtrates, filtration and washing of the precipitate with alcohol, and recovery of the mixed perchlorates of calcium, sodium, and magnesium by distilling off the alcohol. The solid residue is warmed in a basin with sufficient 50% sodium carbonate to convert the mixed salts completely into the sodium compound, the whole filtered, and the filtrate concentrated to crystallisation point. A large excess of 40% hydrochloric acid is added, the clear liquid decanted from the precipitated sodium chloride, the last drops being separated on a vacuum filter, and the solution of sodium perchlorate concentrated to D 1.125. A series of determinations carried out with recovered material gave uniformly higher results than duplicate tests carried

out with pure perchloric acid. Investigation showed that the presence of sodium perchlorate in the recovered material diminishes the solubility of the potassium salt, and that therefore more accurate results are obtained by using the recovered material than by working with chemically pure perchloric acid. S. I. L.

Appearance of Fogs in Chemical Reactions. VIKTOR ROTHMUND (*Monatsh.*, 1918, **39**, 571—601).—The nature of the fogs produced in certain chemical reactions has been investigated. In the case of the fogs produced when ozone enters into reaction with a large number of reagents (particularly reducing agents), it is shown that the fog consists mainly of water in which a small quantity of the products of the reaction are dissolved. These fogs only occur when the reducing agent is of a volatile nature and when the reaction products are soluble in water. The size of the fog particles is practically the same in a number of very different reactions. The approximate diameter as calculated from the rate of subsidence is 10^{-4} cm. The stability of the liquid drops in saturated water vapour is explained by the increased curvature brought about by the solution of the products of the reaction which effect a reduction of the vapour pressure. In the case of ozone and hydriodic acid, a larger value is calculated for the diameter, and this is explained by the formation of hydrogen peroxide. The ammonium chloride fogs, the fogs from fuming acids, fogs produced by the action of radium emanation on sulphur, carbon disulphide, camphor, and iodine, as well as the electrically produced and atmospheric fogs, are also considered. In all cases, the fog produced shows an analogous behaviour to the ozone fogs and generally has drops of about the same size. J. F. S.

The Waters of the Atlantic Ocean on the Argentine Coasts. HERCULES CORTI and HECTOR H. ALVÁREZ (*Anal. Soc. Quím. Argentina*, 1918, **6**, 108—120).—A detailed study of samples of sea-water taken under varying conditions at different places on the Argentine coast.

Extensive tabular statements are given of chemical composition and of general and physico-chemical properties. The methods of analysis adopted are briefly indicated. W. S. M.

Synthesis of Sulphuryl Chloride in Presence of Organic Compounds. GUIDO CUSMANO (*Atti R. Accad. Lincei*, 1918, [v], **27**, ii, 201—204).—The keto-cineole described by the author and Linari (*A.*, 1912, i, 272) is similar in many of its chemical properties to camphor, which it may replace in the preparation of sulphuryl chloride from sulphur dioxide and chlorine by Schulze's method. The reaction, $\text{SO}_2 + \text{Cl}_2 = \text{SO}_2\text{Cl}_2$, is also accelerated by cyclohexanone, menthone, or tetrahydrocarvone, but does not occur in presence of α -bromocamphor, Reyckler's camphorsulphonic acid, camphorquinone, or monobromo- or monochloro-ketocineole (to be described elsewhere) with the halogen attached to the methylene contiguous to the carbonyl group; the reaction is, however,

activated by introducing into the compounds just named a positive radicle, for instance, by transforming the sulphonic acid into either the amide or the anilide, or camphorquinone into the monoxime or isonitrosocamphor. Pernitrosocamphor also catalyses this reaction, but not the anilide of chlorocamphorsulphonic acid. These results are not in disagreement with the view that the catalytic action of camphor is connected with the formation at low temperatures of one or more compounds of sulphur dioxide with camphor.

T. H. P.

New Method for the Synthesis of Ammonia. H. HAMPEL and R. STEINAU (*Chem. Zeit.*, 1918, **42**, 594).—Metallic iron, ammonium chloride, and nitrogen are heated together at 300° under 50 atmospheres pressure. The reaction proceeds according to the equation $3\text{Fe} + 6\text{NH}_4\text{Cl} + 2\text{N} = 3\text{FeCl}_2 + 8\text{NH}_3$. A gaseous mixture is obtained containing up to 99% of ammonia. The portion of this derived from the ammonium chloride may be allowed to react with the ferrous chloride; the ferrous hydroxide formed is reduced and the ammonium chloride recovered for further use. [See, further, *J. Soc. Chem. Ind.*, 1919, February.] W. P. S.

Mixtures of Nitrogen Peroxide and Nitric Acid. WILLIAM ROBERT BOUSFIELD (*T.*, 1919, **115**, 45—55).

Oxidation Pressure Limits (A Theory of the Pressure Limit in Autoxidation). W. P. JORISSEN (*Chem. Weekblad*, 1918, **15**, 705—714).—A résumé of the observations and measurements on the lower limit of pressure in the autoxidation of phosphorus in oxygen, and of the theories which have been advanced to account for the facts observed.

The author considers the phenomenon to be a particular case of the ignition of an inflammable gas mixture (phosphorus vapour and oxygen) whenever the ratio of combustible constituent to oxygen becomes sufficiently large, the temperature in this case being sufficiently high to cause spontaneous ignition. W. S. M.

The Atomic Structure of Carborundum determined by X-Rays. C. L. BURDICK and E. A. OWEN (*J. Amer. Chem. Soc.*, 1918, **40**, 1749—1759).—The angle between the edges of the elementary rhombohedron of carborundum, which crystallises in the ditrigonal pyramidal class of the hexagonal system, is $89^\circ 56' 6''$, the departure from the simple cube being due to a shortening by only 0.15% of one trigonal axis of the cube. The results of the X-ray measurements here recorded, using rays from a palladium target, show a very close relationship between the crystal structure of carborundum and that of diamond. The silicon and carbon atoms in the carborundum crystal are each arranged on face-centred rhombohedral (nearly cubic) lattices. In the prism planes (10 $\bar{1}$ 0) and (11 $\bar{2}$ 0), the carbon and silicon atoms lie in the same planes, from which it follows that in the direction of the principal

axis the carbon and silicon atoms alternate, there being no lateral displacement between the two kinds of atom with respect to this axis. From the relative intensities of the reflections of the spectra of different orders by the different planes, the displacement of the carbon planes from the silicon planes in the direction of the principal axis is calculated to be equal to 0.36 of the distance between two consecutive carbon or silicon planes. The carborundum structure can then be derived from that of the diamond by replacing the carbon atoms of one of the two interpenetrating face-centred cubic lattices of the diamond by a similar lattice of silicon atoms, shortening one trigonal axis by 0.15%, and displacing the atoms of one lattice from a position 0.25 to one 0.36 of the distance between successive planes of the other lattice in the direction of the shortened axis.

From the values of the distances between the atom planes derived from the measurements, the density of carborundum is calculated to be 3.11, the observed value being 3.123. E. H. R.

Electrolysis of Potassium Phosphate. A. RIUS Y MIRÓ (*Anal. Fis. Quim.*, 1918, **16**, 573—610).—The electrolytic oxidation of potassium phosphates is assumed to take place in two stages, the first being the formation of perphosphate and the second that of monoperphosphate. For dipotassium hydrogen phosphate, the primary reaction can be represented by the equation $2K_2HPO_4 + O = K_4P_2O_8 + H_2O$. The perphosphate then undergoes further oxidation to monoperphosphate, $K_4P_2O_8 + O + H_2O = 2K_2HPO_5$.

A. J. W.

The Fusion of Sodium Hydroxide with some Inorganic Salts. MAITLAND C. BOSWELL and J. V. DICKSON (*J. Amer. Chem. Soc.*, 1918, **40**, 1773—1779).—When certain salts which can function as oxygen acceptors are fused at high temperatures (300—400°) with sodium hydroxide, the salt is oxidised and hydrogen evolved. Quantitative experiments have been made with sodium arsenite and ferrous sulphate, and it is found that the hydrogen given off is equivalent to the oxygen taken up by the salt. Stannous chloride and vanadium sulphate are also oxidised, and cerous and uranous sulphates to a small extent. It is remarkable that such readily oxidisable salts as sodium nitrite and sodium sulphite are not oxidised when fused with sodium hydroxide. It is perhaps noteworthy that all the bases the salts of which were found to be oxidised belong, with the exception of iron, to groups 4, 5, or 6 of the periodic table.

The mechanism of the reaction consists ultimately in the decomposition of water, the oxygen carrying the oxygen acceptor to a higher stage of oxidation, whilst the hydrogen is evolved as gas. The general oxidising action of water catalysed by sodium hydroxide is also shown by the evolution of hydrogen when such metals as zinc and aluminium are boiled with sodium hydroxide solution.

E. H. R.

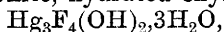
Some Properties of Magnesium Ammonium Phosphate and Magnesium Pyrophosphate. Z. KARAOGLANOV and P. DIMITROV (*Zeitsch. anal. Chem.*, 1918, 57, 353—371).—The conversion of magnesium ammonium phosphate into magnesium pyrophosphate by ignition sometimes is and sometimes is not accompanied by incandescence. The presence or absence of the phenomenon is found to depend on the conditions under which the magnesium ammonium phosphate is precipitated. If precipitated slowly at the boiling temperature, the product does not incandesce, but if formed quickly at lower temperatures, it invariably does, whether precipitated from a magnesium solution or from a phosphoric acid solution. The pyrophosphate formed with incandescence is grey to black in colour, whilst that formed without incandescence is quite white. The authors conclude from their experiments that only samples of magnesium ammonium phosphate which contain traces of organic matter will incandesce on ignition, since when organic matter, such as filter paper, is carefully excluded, no incandescence is observed. There are apparently two modifications of magnesium pyrophosphate, differing considerably in physical properties. The one, formed without incandescence, is loose in texture and white in colour; the other, the formation of which is always accompanied by incandescence, is hard and lava-like, grey to black in colour, and more resistant to hydrochloric and nitric acids. Its colour is due to enclosed particles of carbon, and is only with difficulty removed at a very high temperature by ignition, but can be destroyed by treatment with acids or an oxidising agent, such as ammonium nitrate. The incandescence of any sample of magnesium ammonium phosphate can be prevented by evaporating it before ignition with an ammonium salt or by heating very slowly to the decomposition temperature. The opinion of Balareff (*A.*, 1917, ii, 90) that the properties of the magnesium pyrophosphate obtained depend on the vapour tension (degree of hydration) of the magnesium ammonium phosphate before calcination is shown to be incorrect. E. H. R.

Adsorption of Metals from Drinking Water by Glass. K. SCHERINGA (*Pharm. Weekblad*, 1919, 56, 8—9).—The proportion of lead in drinking-water can considerably diminish within a few hours. It is known that if an aqueous magenta solution be boiled in a glass vessel, the latter cannot afterwards be cleaned in the ordinary way; this absorption, however, does not occur if the vessel has been previously cleaned carefully with soap and water and afterwards well rinsed out. Since, then, organic dyes are not adsorbed by a cleaned glass surface, it appears very doubtful that metallic salts should be so adsorbed. This conclusion was confirmed by estimating colorimetrically solutions of various salts which had been allowed to remain for two days in carefully cleaned glass vessels. In no case was the slightest diminution of the amount of metal in solution detected. It appears, therefore, that the diminution in the case of lead is due to chemical action, either

by disturbance of an equilibrium when the water is removed from contact with the lead, or by precipitation of finely divided lead carbonate.

S. I. L.

Anhydrous Mercuric Fluoride. OTTO RUFF and GUSTAV BAHLAU (*Ber.*, 1918, **51**, 1752—1760).—*Anhydrous mercuric fluoride* may be prepared by heating mercurous fluoride in a current of dry chlorine at 275°, or of dry bromine at 400°, or by heating mercurous fluoride at 450° under 10 mm. pressure. Mercuric fluoride forms transparent, octahedral crystals, m. p. 645°; its b. p. is estimated at 650°. It has D^{15}_4 8.95. Attempts to determine the vapour tension at various temperatures did not yield satisfactory results, since the vessels are attacked by the vapours. The substance is very sensitive to moisture and becomes discoloured by traces of water vapour, which are not analytically demonstrable; on exposure to air, hydrogen fluoride is evolved, and mercuric oxyfluoride and, ultimately, mercuric oxide, remain. With small quantities of water, a white, hydrated oxyfluoride,



is formed, whilst with larger quantities, mercuric oxide is gradually produced. Mercuric fluoride dissolves in hydrofluoric acid solution (40%), and, on cautious evaporation, the hydrated fluoride, $\text{HgF}_2 \cdot 2\text{H}_2\text{O}$, is obtained in small, colourless crystals. The vapours of mercuric fluoride attack platinum above 500°; mixtures of the fluoride with silver, copper, lead, aluminium, magnesium, zinc, tin, chromium, iron, or arsenic react vigorously when strongly heated locally, yielding amalgams and metallic fluorides, the latter being easily isolable in the pure condition if an excess of mercuric fluoride is used. Sulphur tetrafluoride appears to be formed when mercuric fluoride is heated with sulphur, but no reaction occurs with amorphous or graphitic carbon. The fluorine does not appear to be replaced when the fluoride is heated in a stream of chlorine or bromine.

Mercuric chlorofluoride, HgClF , is obtained as a pale yellow substance by passing dry chlorine over mercurous fluoride at 120°; the pale yellow *bromofluoride* is similarly prepared at 105°.

The preparation of mercuric fluoride in quantity is best effected by the process first described.

H. W.

Double Catalytic Process in the Oxidation of Aluminium in the Presence of Mercury. Oxidation of Aluminium Powder at the Ordinary Temperature. P. RONCERAY (*Bull. Sci. Pharmacol.*, 1918, **25**, 193—198; from *Chem. Zentr.*, 1918, ii, 699).—Aluminium in a fine state of division is oxidised by the air and under water. Pieces of aluminium in contact with iron do not oxidise in water, but in the presence of a small quantity of mercury, aluminium undergoes oxidation through the operation of two catalytic processes. The mercury, owing to the formation of an amalgam, reduces the aluminium to a molecular state, and the mercury oxide produced acts as an agent for the transfer of

oxygen from the air to the aluminium. Pieces of aluminium after rubbing with mercury oxide are rapidly oxidised in the air and under water.

H. W. B.

Solubility of Aluminium Hydroxide. E. H. ARCHIBALD and Y. HABASIAN (*Trans. Roy. Soc. Canada*, 1917—1918, [iii], **11**, 1—6).—The solubility of aluminium hydroxide in ammonia solutions of different concentrations and in similar solutions to which various amounts of ammonium or potassium nitrate had been added, has been determined at 20° and 30°. The method consisted in shaking the freshly precipitated hydroxide in sealed tubes with the solvent for twelve hours in a thermostat, filtering, evaporating measured weights of the solution in a platinum crucible, igniting, and weighing. The following weights of $\text{Al}(\text{OH})_3$ dissolve in 100 c.c. of solution of ammonia at 20°:

Normality of NH_4OH , 0.050, 0.100, 0.125, 0.200, 0.500, 1.00.

Grams of $\text{Al}(\text{OH})_3$, 0.0070, 0.0080, 0.0250, 0.0380, 0.0450, 0.0240.

The solubility increases, therefore, with the ammonia concentration to a maximum which lies at 0.5*N*-ammonia, and then decreases. In these experiments, it is shown that the amount of aluminium hydroxide in solution after thirty minutes' shaking is considerably more than the above quantity, but decreases as the shaking proceeds until equilibrium is reached, which is always achieved in less than twelve hours. The presence of ammonium nitrate decreases the solubility of aluminium hydroxide in ammonia, and the decrease is greater the higher the temperature and the concentration of ammonium nitrate. The addition of potassium nitrate increases the solubility of aluminium hydroxide to a very marked extent. It is pointed out that in the quantitative estimation of aluminium, only a small excess of ammonia should be used, and a 10% solution of ammonium nitrate should be used in the washing.

J. F. S.

Relation between Molecular Structure and the Activity towards Hydrogen Sulphide of Oxide of Iron. G. WEYMAN (*J. Soc. Chem. Ind.*, 1918, **37**, 333—336r).—Iron oxides obtained by heating at 100° to 650° are equally active as regards absorption of hydrogen sulphide in the cold, but at 750° a change occurs, which may also be effected at lower temperatures by very prolonged heating. It seems that the activity of the oxide is dependent primarily on molecular structure, and not on any particular degree of hydration, but the oxide is derived in almost all cases from some form of hydrate.

W. P. S.

Chromatocobaltiammines. SAMUEL HENRY CLIFFORD BRIGGS (*T.*, 1919, **115**, 67—76).

The Evolution and Oxidation of Chromic Hydroxide in Alkaline Solution. F. BOURION and A. SÉNÉCHAL (*Compt. rend.*, 1919, **168**, 59—62).—An alkaline solution of chromic hydroxide

undergoes a change on keeping, which tends to make it lose its chemical activity, particularly in respect to its powers of reducing hydrogen peroxide. This change is the more rapid as the concentration of the chromium is greater and of the alkali is smaller. It is, however, possible to oxidise 97% of the chromium in chrome alum to chromate by adding sodium hydroxide to the solution of the alum containing four times the calculated quantity of hydrogen peroxide, and then immediately destroying the excess of peroxide by shaking the solution with manganese dioxide. W. G.

The Crystalline Structure of Grey Tin. A. J. BIJL and N. H. KOLKMEIJER (*Chem. Weekblad*, 1918, **15**, 1264).—A preliminary note on the crystalline structure of grey tin. The authors have shown that the crystals belong to the regular system.

W. S. M.

Bismuth Hydride and Polonium Hydride. FRITZ PANETH (*Ber.*, 1918, **51**, 1704—1728).—By application of the methods used in the study of radioactive substances, the author has succeeded in demonstrating that bismuth forms a gaseous hydride which possesses considerable stability at the ordinary temperature and is not decomposed with much greater readiness than antimony hydride; with increasing temperature, the substance rapidly becomes less stable, and is decomposed into its elements at a red heat. The gas can be almost completely condensed by the use of liquid air, and subsequently, in part, regasified.

Bismuth hydride is obtained by the solution of an alloy of magnesium with thorium-*C* or radium-*C* in 0.2*N*-hydrochloric or sulphuric acid. The alloy is prepared by exposing magnesium foil to the radiations of a radiothorium preparation contained in a glass capsule covered with silk paper, which is impermeable to thorium-*X*; shortly after its removal, in consequence of the rapid decay of thorium emanation and thorium-*A*, the deposit consists entirely of thorium-*B* and thorium-*C*. The alloy is placed in a weighing bottle connected with an electroscope in such a manner that a regular current of nitrogen can be sent through the apparatus. After determination of the natural leak of the electroscope, 0.2*N*-hydrochloric acid is dropped on to the alloy; the electroscope soon indicates an activity, which becomes feebler after a few minutes. The results of this and similar experiments show that when magnesium superficially alloyed with bismuth and lead is dissolved in dilute hydrochloric acid, a few thousandths of the bismuth are converted into such a state that they can be carried by a gas current through a cotton wool filter, and that a similar reaction does not occur with lead. A series of control experiments shows that the observed effects are actually due to a volatile compound of bismuth, and not, for example, to the liberation of thorium-*C*, to the selective action of the filter, or to the relatively greater volatility of thorium-*C* chloride.

Polonium hydride is prepared in a similar manner. The alloy

of magnesium and polonium is prepared by the electrolysis of a feebly acid solution of polonium chloride, a piece of magnesium foil being used as cathode. When the alloy is dissolved in dilute acid and the gases evolved are led into an electroscope, an activation is observed which does not decrease in the course of a day, and therefore is caused by polonium. The gas closely resembles bismuth hydride. It is remarkable that a current of oxygen can be used instead of hydrogen or nitrogen for the transport of the gas without sensibly diminishing the yield. The latter is less than in the case of bismuth hydride, and up to the present it has not been found possible to convert more than a few tenths' part per thousand of the polonium into the gaseous state. If the gas current is cooled to -84° , the polonium hydride is only partly condensed. The investigation of the gas is rendered very tedious, since in each experiment the electroscope becomes permanently damaged and does not recover when left to itself for a time.

H. W.

Bismuth Hydride. II. FRITZ PANETH and ERICH WINTERNITZ (*Ber.*, 1918, 51, 1728—1743).—The application of radioactive methods having shown that bismuth hydride is capable of existence, and having indicated its mode of preparation and general properties (preceding abstract), the authors now describe attempts to prepare it in weighable quantity from non-radioactive material.

The requisite bismuth-magnesium alloy is prepared by heating equal weights of powdered bismuth and magnesium (as free from silicon as possible) in an iron crucible in a rapid stream of dry hydrogen. The alloy is dissolved in approximately 4*N*-hydrochloric or sulphuric acid (or in some cases nitric acid). Bismuth hydride is thus obtained in sufficient quantity to permit its detection either by the formation of a bismuth mirror or by luminescence tests.

The bismuth mirror is obtained in the usual Marsh's apparatus, and very closely resembles the antimony mirror. As generally obtained, it consists of a strong brown ring in front of and a fainter ring behind the heated spot. The former deposit appears to be frequently burnt into the glass and to be unsuitable for further experiments. This drawback can be overcome by placing a pierced clay disk on the tube and allowing the flame to play against this, as also by increasing the velocity of the gas current. The antimony, arsenic, and bismuth mirrors are most readily distinguished by a number of chemical tests involving the use of sodium hypochlorite, yellow ammonium sulphide, hydrogen sulphide, etc., which are fully described in the original. Attempts to estimate the yield of bismuth hydride by weighing the bismuth mirrors show that about 5×10^{-5} of the bismuth used is converted into the hydride, or that the yield is only about one-twentieth of that obtained from thorium-C. It should be noted, however, in this connexion that circumstances have prevented the authors from determining the optimum conditions of experimenting.

The authors have also applied Donau's luminescence method (A.,

1913, ii, 743) to the detection of traces of bismuth, and find the procedure very rapid and so sensitive that it is capable of proving the presence of traces of bismuth which cannot be detected by the ring test. For this purpose, the gases issuing from the Marsh's apparatus are ignited, and a piece of pure calcium carbonate is held on a platinum loop in the flame; the bismuth hydride is decomposed, and a portion of the bismuth is deposited on the lime. The latter is allowed to cool, and then placed at the edge of the hydrogen flame, when the presence of bismuth is betrayed by the cornflower-blue luminescence; in similar circumstances, antimony is readily detected by a sky-blue luminescence, both colorations being readily visible in bright daylight.

The absorption of bismuth hydride by various reagents has been examined; the most suitable solution for this purpose appears to be 0.4*N*-silver nitrate solution. Water absorbs the gas to some degree, and 4*N*-sulphuric acid to about the same extent. 0.5*N*-Sodium carbonate solution and *N*-potassium hydroxide solution are more active, whilst the gas is also absorbed by desiccating agents, such as calcium chloride or soda-lime. It is completely decomposed by concentrated sulphuric acid. An aqueous solution of hydrogen sulphide is not more efficient than pure water.

H. W.

Gold Amalgams. N. PARRAVANO (*Atti R. Accad. Lincei*, 1918, [v], **27**, ii, 168—170; *Gazzetta*, 1918, **48**, ii, 123—128).—Objections are raised to the argument of Guertler (*Metallographic*, 524), who concludes that mercury dissolves in gold, giving origin to a solid solution containing at most about 10% of gold, and that in the amalgams containing 90—0% of gold no other crystalline individual is formed. The author has made the following experiments: (1) Definite quantities of saturated amalgam and of gold are placed in a vessel, and the latter exhausted; distillation of the mercury on to the gold then proceeds until the composition of the amalgam formed reaches that of the solid in equilibrium with the liquid amalgam. (2) A current of hydrogen is passed over the amalgam; the quantity of mercury thus transported will be a function of the tension of the mercury of the amalgam provided that, in any series of experiments, the form of the apparatus and the velocity and duration of the gaseous current are maintained constant. The results show that gold amalgams contain at least the two compounds Au_2Hg_3 and Au_3Hg .

T. H. P.

Amalgams. I. Colloidal Gold Amalgam. C. PAAL and HERMANN STEYER (*Kolloid Zeitsch.*, 1918, **23**, 145—158).—Hydrosols of gold amalgam have been prepared (1) by shaking gold sols with metallic mercury, (2) by allowing a gold sol to remain in contact with metallic mercury at rest, (3) by mixing solutions of gold hydrosol with mercury hydrosol, and (4) by precipitating both gold and mercury from a solution of the mixed chlorides in the presence of a protecting colloid. In the last-named case, amalgam hydrosols

of the composition represented by the formulæ Au_3Hg_2 and Au_2Hg_3 were prepared by reducing a mixture of suitable concentration of the two chlorides in alkaline solution by hydrazine in the presence of the sodium salts of protalbic and lysalbic acids. The solutions after dialysis were evaporated to dryness in a vacuum, and gave brittle substances which possessed a black or greenish-black colour and a metallic lustre. These substances readily dissolved in water with the production of colloidal solutions. The stability, composition, and general properties of the hydrosols varied with the method of preparation.

J. F. S.

Solubilities of Ammonium Platinichloride, Platinibromide, and Iridichloride and the Separation of Platinum and Iridium. E. H. ARCHIBALD and JOHN W. KERN (*Trans. Roy. Soc. Canada*, 1917—1918, [iii], 11, 7—16).—The solubility of the ammonium salts of chloroplatinic, bromoplatinic, and chloroiridic acids has been determined at a series of temperatures in water and in solutions of various strengths of ammonium chloride and ammonium bromide. It is shown that 100 grams of water dissolve 0.2902 gram of ammonium platinichloride at 0.1° , 0.3652 gram at 7.2° , 0.4869 gram at 18.0° , 0.5760 gram at 25.4° , 0.6370 gram at 29.9° , 0.7870 gram at 38.9° , 1.0131 grams at 49.7° , 1.4740 grams at 60.2° , 1.7440 grams at 70.0° , 2.1800 grams at 80.2° , 2.6150 grams at 90.0° , and 3.2515 grams at 99° . Ammonium platinibromide is somewhat more soluble in water than the foregoing salt; 100 grams of water dissolve 0.4165 gram at 0.2° , 0.5002 gram at 7.3° , 0.6438 gram at 19.0° , 0.7384 gram at 25.0° , 0.8147 gram at 29.7° , 1.0355 grams at 40.0° , 1.2087 grams at 50° , 1.5780 grams at 60.0° , 1.9265 grams at 70.0° , 2.3002 grams at 80.0° , 2.8370 grams at 90° , and 3.5866 grams at 99° . Ammonium iridichloride is much more soluble than either of the platinum compounds; 100 grams of water dissolve 0.5661 gram at 0.2° , 0.7055 gram at 10.0° , 1.0910 grams at 25.0° , 1.2066 grams at 30.0° , 1.5665 grams at 40.0° , 1.9664 grams at 50.0° , 2.4567 grams at 60.0° , and 4.3815 grams at 80.0° . In the presence of ammonium chloride, the solubility of the ammonium salts of chloroplatinic acid and chloroiridic acid is much reduced, but that of the iridichloride is several times as large as that of the platinichloride. Ammonium bromide reduces the solubility of the platinibromide. In all three cases, the reduction in the solubility is proportional to the concentration of the ammonium haloid. The difference in the solubility of ammonium platinichloride and iridichloride furnishes a good method for the complete separation of platinum and iridium. Ammonium platinichloride is appreciably less soluble than potassium platinichloride.

J. F. S.

Dehydrogenation of Palladium Hydrogen Hydrosol by Metallic and Colloidal Mercury. C. PAAL and HERMANN STEYER (*Ber.*, 1918, 51, 1743—1752).—It has been previously shown (Paal and Hartmann, A., 1918, ii, 303) that palladium

hydrosol gradually loses its catalytic activity in the presence of metallic or colloidal mercury; in the course of experiments on the action of the hydrosol on mixtures of hydrogen and oxygen in the presence of mercury, it was observed that the catalyst speedily became passive and that the gradual slight absorption of hydrogen was preceded by a temporary increase in the volume of the latter. This phenomenon forms the subject of the present communication, in which it is demonstrated that the palladium hydrogen hydrosol is decomposed by mercury with evolution of hydrogen, and that dehydrogenation is effected more rapidly by metallic than by colloidal mercury. Analysis of the residual palladium hydrosol and of the mercury proves that a portion of the palladium has passed into the mercury, and that some of the latter has passed into the hydrosol. The action of colloidal mercury on palladium hydrogen hydrosol only leads to uniform results when care is taken that only the least possible excess of hydrazine is used as reducing agent in the formation of the mercury hydrosol.

H. W.

Mineralogical Chemistry.

Mineralogy of the H.B. Mine, Salmo, British Columbia.
T. L. WALKER (*Toronto Univ. Studies, Geol. Ser.*, No. 10, 1918, reprint, 25 pp.).—The oxidised zinc-lead ores of this mine consist of a mixture of hemimorphite, cerussite, and limonite, and occur as bedded "veins" in metamorphosed limestone, with associated quartzite and schists, and penetrated by dykes of minette. A cave in the mine contains also a number of zinc phosphate minerals forming large stalactitic pillars, which yielded about a hundred tons of ore. These stalactites consist mainly of a core of spencerite with a thin crust of hemimorphite, and between the two, solution cavities containing crystals of hemimorphite (anal. I, deducting 6.66% calcite), spencerite, hopeite, parahopeite (anal. II, D 3.236), and hibbenite. Crystallographic descriptions are given of each of these minerals, except the hibbenite, the existence of which is not confirmed. On the floor of the cave, and partly coating the stalactites, is a deposit of a grey or cream-coloured, non-plastic, zinciferous clay (anal. III), resembling the so-called moresnetite and vanuxemite in composition, but doubtless a mixture of some zinc mineral with clay. The phosphoric acid of these minerals was perhaps derived from the solution of apatite in the surrounding rocks.

	ZnO.	MgO.	Al ₂ O ₃ .	Fe ₂ O ₃ .	SiO ₂ .	P ₂ O ₅ .	H ₂ O.	Total.
I.	87.35	—	—	—	25.32	—	7.33	100.00
II.	54.69	—	—	—	—	30.46	15.31	100.46
III.	19.99	3.97	16.07	8.01	39.49	0.26	11.12	98.91

The zinc phosphate minerals now known are the following; they

are all remarkable for their chemical purity, there being a complete absence of elements not shown in the formulæ:

Hopeite.....	$\text{Zn}_3(\text{PO}_4)_2, 4\text{H}_2\text{O}$, orthorhombic	} (A., 1908, ii, 397).
Parahopeite	$\text{Zn}_3(\text{PO}_4)_2, 4\text{H}_2\text{O}$, triclinic	
Tarbuttite	$\text{Zn}_3(\text{PO}_4)_2, \text{Zn}(\text{OH})_2$, triclinic	
Spencerite	$\text{Zn}_3(\text{PO}_4)_2, \text{Zn}(\text{OH})_2, 3\text{H}_2\text{O}$, monoclinic	(A., 1916, ii, 629).
Hibbenite.....	$2\text{Zn}_3(\text{PO}_4)_2, \text{Zn}(\text{OH})_2, 6\frac{1}{2}\text{H}_2\text{O}$, orthorhombic	(A., 1916, ii, 569).

L. J. S.

Examination of the Hot Springs at Banff, Alberta.

R. T. ELWORTHY (*Trans. Roy. Soc. Canada*, 1917—1918, [iii], 11, 27—33).—An analysis of the water of, and the gases evolved from, the six hot springs at Banff, Alberta, has been carried out. The upper hot spring contains the following amounts of dissolved solids in parts per million of water: 634, SO_4 ; 10, Cl; 133, HCO_3 ; 239, Ca; 39.7, Mg; 9.1, alkalis; 31, SiO_2 . The total solids amount to 1100 parts per million. Among other metals present are iron, aluminium, manganese, strontium, magnesium, lithium, potassium, and sodium. The gases evolved by the springs contained methane, hydrogen, oxygen, carbon dioxide, nitrogen, helium, and argon. Full analyses are recorded in the paper. These springs are the most radioactive of any yet examined in Canada, the emanation content of the gas being $(1910\text{—}2370) \times 10^{-12}$ curies per litre whilst that of the water is $(221\text{—}640) \times 10^{-12}$ curies per litre. The dissolved radium is $(8.5\text{—}23.5) \times 10^{-12}$ grams per litre. J. F. S.

The Thermal Mineral Springs of Río Hondo. HÉRCULES CORTI (*Anal. Soc. Quím. Argentina*, 1918, 6, 215—229).—A detailed account of the medicinal properties and chemical composition of the thermal springs of Río Hondo, in the province of Santiago del Estero in the Argentine. W. S. M.

Analytical Chemistry.

Rational Approximated Atomic Weights for Use in Chemical Analysis. N. SCHOORL (*Chem. Weekblad*, 1918, **15**, 547—562; *Zeitsch. anal. Chem.*, 1918, **57**, 209—225).—In ordinary analytical work, it is customary to use for the atomic weights values given to the nearest decimal figure corresponding with the degree of accuracy possible for each determination. In 1904, Erdmann proposed to use atomic weights calculated from hydrogen as unity, since most of the values were very close to whole numbers. Since, however, the atomic weights of one or two of the commonest elements cannot be rounded off to whole numbers without introduction of considerable error, the proposal has found little favour.

The author puts forward the consideration that much more satisfactory values are obtained for analytical purposes by taking account of the fact that, whereas in all accurate atomic weight determinations the weighings are reduced to the proper values for weighing in a vacuum, in analytical work the correction for the weight of air displaced is seldom made. He proposes to use a set of "air atomic weights" obtained from the accepted atomic weights by introducing values based on the air correction. The accepted atomic weight of iodine is, for example, 126.92. Allowing for the difference in specific gravity of iodine and the brass weights generally used in chemical analysis, the volume atom of iodine, namely, 126.92 grams weighed in a vacuum, would weigh in air 126.906 grams. Though the value of this air correction is so small as generally to affect only the third decimal place, it becomes much greater in the cases of carbon, hydrogen, and oxygen, the elements chiefly concerned in organic analysis. The atomic weight of hydrogen is given by the International Committee for 1916 as 1.008. Assuming the atomic volume of hydrogen in combination to be 6, the "air atomic weight" becomes 1.0005, which can without any inaccuracy be given as 1.00 for ordinary purposes. The correction for oxygen, assuming an atomic volume of 6, does not alter the accepted value 16.00, whilst carbon with the accepted atomic weight of 12.005 becomes 11.999, that is, for ordinary purposes 12.00. Similarly, the "air molecular weight" of water becomes 18.00 instead of 18.02 on the basis of the true atomic weights.

The values given in the International table of atomic weights for 1916 have been modified to give the air atomic weights for analytical purposes on the basis of the atomic volumes of the elements. The author devotes many pages to a selection of suitable atomic volumes for each element, basing his calculations on Kopp's law that the atomic volumes are additive. In the case of most of the elements, the values adopted for the atomic volumes are averages of very different figures; the values for cobalt, for example, deduced from the oxide, chloride, bromide, sulphide, and sulphate, respectively, are 7, 9, 2, 1, and 4, the average value, 5, being adopted. As the basis for the calculations for obtaining the atomic volumes of the elements from the specific gravities of their compounds, the following atomic volumes are assumed: O=6, S=16, Cl=15, Br=22, I=31. The atomic volumes of the halogens and of the alkali and alkaline earth metals are taken as approximately half of the values deduced from the atomic weights and the specific gravities.

In order to obtain trustworthy figures for molecular and equivalent weights for ordinary analysis, it is suggested that use may be made of the true molecular volumes of the commoner reagents. The molecular weight of oxalic acid, for example, is 126.058, calculated from the accepted atomic weights. The specific gravity being 1.64, the value to be subtracted to arrive at the "air molecular weight" is 0.076, giving the value for use in volumetric analysis as 125.982. By addition of the air atomic weights given in the

table, the value 125.976 is obtained, which agrees with the figure of 125.982 obtained from the molecular volume better than does the figure 126.058 obtained by addition of the accepted atomic weights. This argument is repeated for the various reagents used in iodine determinations. It is shown, also, that in analysis of organic compounds for the elements, use of the "air atomic weights" would reduce the hydrogen content by nearly 1% of its value, and since in analysis the hydrogen content as a rule is somewhat too high, it is contended that the use of the "air atomic weights" will give more accurate results. S. I. L.

The Importance of Electrical Conductivity in Analytical Chemistry. I. M. KOLTHOFF (*Chem. Weekblad*, 1918, 15, 889—896).—The determination of conductivity can be employed in a great number of cases as an aid in quantitative analysis, and is very simply and easily carried out. The author has indicated a few cases of the application, leaving to later papers the detailed account and the theoretical discussion. The general cases that arise in volumetric work can be divided into two classes: (1) reactions in which all the ions remain in solution; in this case, the conductivity will generally increase; (2) reactions in which ions disappear. In the second class, the conductivity may (a) diminish, (b) remain unaltered, (c) increase. Suppose a material CD to be added in solution to a solution of AB , and suppose AD to be precipitated as a result of the reaction; the nett result is that in the original solution the B ions remain, whilst the A ions are replaced by C . If the specific conductivity of A is greater than that of C , the conductivity will rise; this occurs, for example, in the neutralisation of a strong acid by a base, the H ion being replaced by the ion of the metal of the base. In the titration of hydrochloric acid by means of sodium hydroxide, for example, the conductivity falls rapidly until all the acid is neutralised; if more alkali be added, the conductivity begins sharply to increase. By plotting the conductivity of the solution against the quantity of alkali is added, the conductivity begins sharply to increase. By neutral point of minimum conductivity The application would be of great use, for example, with a strongly coloured solution for which no colour indicator could be used.

If, in the above cases, the conductivity of A is equal to that of C , which may happen when a precipitate is formed, the conductivity will change very little until the reaction is complete, after which further addition of the second solution causes a rapid increase. Here, also, the measurement can be of importance for analysis, especially where the precipitate forms slowly or is microcrystalline. In the case of neutralisation of weak acids or bases, the conductivity generally increases during the titration, since the slightly dissociated acid is replaced by a highly dissociated salt. Further addition of the base causes a sharp rise in the conductivity, by reason of the presence of the hydroxyl ion. If the values are plotted, the neutral point can easily be determined, and the method

is of wide application in this case, since colour indicators are not available with weak acids and bases.

Further applications are, for example, titration of a weak acid in the presence of a strong acid, determination of the combined alkali in a salt of a weak acid, determination of basic or acidic properties of a substance, as, for example, the acid character of hydrogen peroxide, etc. Similarly, the concentration of an electrolyte can be determined from the conductivity with the help of tables, and determinations of conductivity combined with specific gravities or other physical constants can be used for analysis of a mixture of two electrolytes. In food analysis, also, the determination may be of great use.

S. I. L.

The Effect of Dilution in Electro-titrimetric Analyses.
GILBERT ARTHUR FREAK (T., 1919, 115, 55—61).

The Quinone Phenolate Theory of Indicators. Spectrophotometric Study of the End Points and Fading of Phenolsulphophthalein Indicators. CHARLES L. BRIGHTMAN, J. J. HOPFIELD, M. R. MEACHAM, and S. F. ACREE (*J. Amer. Chem. Soc.*, 1918, 40, 1940—1944).—The present communication deals with phenolsulphophthalein and its tetrabromo- and tetranitro-derivatives. It is found that these indicators have a number of properties which make them the best series yet developed. They are twice as deeply coloured as phenolphthalein in alkaline solution and show sharper colour changes. The excess of alkali necessary to produce the end-point of the neutralisation of the indicator does not cause any appreciable fading in either short- or long-time periods in the case of phenolsulphophthalein and its tetrabromo-derivative. The colour of phenolsulphophthalein in phosphate buffer solutions does not fade appreciably even in considerable periods of time.

Standardised stock solutions of phenolsulphophthalein can be kept in an ice-box without appreciable change, or even at ordinary temperatures if care is taken to prevent contamination, and will then show the same absorption index when treated with an excess of alkali at different time periods. Different samples of the same lot of solid phenolsulphophthalein will give the same absorption index when treated with an excess of alkali.

An excess of alkali in solutions of tetranitrophenolsulphophthalein causes a fading of the intense red colour to a light yellow, the time of fading depending on the amount of alkali and other experimental conditions.

Details of the experimental methods are promised in a subsequent paper

H. W.

The Elimination of the Volume of a Precipitate. H. D. STEENBERGEN (*Chem. Weekblad*, 1918, 15, 1268—1269).—It is sometimes convenient, in order to avoid the washing of a precipitate, to make the estimation of a soluble constituent of a solu-

tion in presence of the precipitate. This may be done by diluting the mixture to two known volumes and estimating the concentration of the solution in each case. A simple formula involving the concentrations thus found is given for the correction required for the volume occupied by the precipitate. W. S. M.

The Significance of the Electrical Conductivity in the Analysis of Potable Water. I. M. KOLTHOFF (*Chem. Weekblad*, 1918, **15**, 1160—1183).—The determination of the electrical conductivity has been used by Reichert, Kohlrausch and Holborn, and others as a rapid method for estimating the total solid constituents in ordinary potable waters. For this purpose, a mean equivalent weight and a mean equivalent conductivity are assumed. The author shows how untrustworthy are the results obtained by this method with different types of water. A series of measurements on the conductivity of dilute aqueous solutions of those salts which are ordinarily present in drinking-water, such as sodium hydrogen carbonate, chloride and sulphate, potassium nitrate, calcium chloride and sulphate, magnesium chloride, etc., and of binary mixtures of these, establishes the rule that the degree of dissociation of each salt in the mixed solution is that which corresponds with the total concentration of electrolyte, even in the case where the salts have no common ion. By means of this rule, the author has prepared tables which permit the calculation of the equivalent conductivity of a mixture when the chemical composition of the solution is known. The comparison of the calculated and the measured conductivities of a water affords a check on the chemical analysis. W. S. M.

Chlorometry. OCTAVE LECOMTE (*Bull. Sci. Pharmacol*, 1918, **25**, 217—218; from *Chem. Zentr.*, 1918, ii, 762—763).—The author estimates the active chlorine in bleaching powder or in hypochlorites by titrating a known quantity of stannous chloride with *N*/10-potassium permanganate first with and then without the addition of the hypochlorite solution. H. W. B.

Detection of Hydrogen Chloride in Chloroform. D. VORLÄNDER (*Ber. deut. Pharm. Ges.*, 1918, **28**, 385—388).—Neutral chloroform when shaken with a very small quantity of dimethylaminoazobenzene gives a yellow-coloured solution; if the chloroform contains a trace of free hydrochloric acid, the yellow coloration changes to violet-red. Carbon dioxide and anhydrous formic and acetic acids, in chloroform solution, do not give a red coloration with dimethylaminoazobenzene. [See, further, *J. Soc. Chem. Ind.*, 1919, 55A.] W. P. S.

Volumetric Estimation of the Sulphion. R. HOWDEN (*Chem. News*, 1918, **117**, 383).—A rapid, approximate method for the estimation of soluble sulphates of the alkali metals in solution is based on their decomposition by barium carbonate. The solution is shaken with pure precipitated barium carbonate in

presence of phenolphthalein, and standard hydrochloric acid is then run in until the red colour is discharged. The solution is filtered and the titration completed on the filtrate, using methyl-orange as indicator. The addition of acid before filtration appears to be necessary to complete the decomposition of the soluble sulphate by the barium carbonate. [See also *J. Soc. Chem. Ind.*, 1919, 57A.] E. H. R.

Folin's Direct Nesslerisation Method for the Estimation of Nitrogen. LOVELL LANGSTROTH (*J. Biol. Chem.*, 1918, **36**, 377—380).—Accurate results are obtained even when impure sulphuric acid is employed for the digestion provided the necessary corrections are made, the latter being ascertained by control blank experiments (compare Folin and Denis, A., 1916, ii, 573).

H. W. B.

Estimation of Phosphorus by the Nephelometric Method. EDWARD B. MEIGS (*J. Biol. Chem.*, 1918, **36**, 335—346).—Accurate estimations of phosphorus by means of the strychnine molybdate reagent (compare Kober and Egerer, A., 1915, ii, 794) can only be obtained by adhering strictly to the prescribed procedure. H. W. B.

Action of Iodine on Hypophosphorous Acid and Phosphorous Acid. Application to the Estimation of Hypophosphites and Phosphites. BOYER and BAUZIL (*J. Pharm. Chim.*, 1918, [vii], **18**, 321—334).—In sulphuric acid solution, iodine oxidises hypophosphorous acid to phosphorous acid according to the equation $\text{H}_3\text{PO}_2 + \text{I}_2 + \text{H}_2\text{O} = \text{H}_3\text{PO}_3 + 2\text{HI}$. This reaction requires about ten hours for completion. The oxidation proceeds a stage further if the solution is treated with an excess of sodium hydrogen carbonate, the phosphorous acid being then converted into phosphoric acid, $\text{H}_3\text{PO}_3 + \text{I}_2 + \text{H}_2\text{O} = \text{H}_3\text{PO}_4 + 2\text{HI}$. In this case, two hours' contact is required, and the mixture must be acidified with acetic acid before the excess of iodine added is titrated. [See, further, *J. Soc. Chem. Ind.*, 1919, February.]

W. P. S.

A Modified Scheibler Apparatus for the Estimation of Carbon Dioxide. M. J. VAN'T KRUYD (*Chem. Weekblad*, 1918, **15**, 870—872).—In order to meet the need for a Scheibler apparatus at the Agricultural Testing Station at Maastricht, and in view of the shortage of rubber in Holland, a modification of the original apparatus has been made. The rubber bag and the three-necked bottle in which this is contained between the reaction flask and the gas-measuring apparatus have been removed. The error which would have been caused had the carbon dioxide evolved been allowed to come into contact with the water in the measuring vessel is obviated by using water saturated with carbon dioxide.

In its modified form, the apparatus is found to give more accurate results than in the original form. S. I. L.

Estimation of Carbon Dioxide in Carbonates. DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1918, **36**, 351—354).—The carbonate, either pulverised or in solution, is placed at the bottom of a test-tube, 20 to 25 mm. in diameter, which is placed in a 250 c.c. suction flask containing an excess of $N/10$ -barium hydroxide solution. A rubber stopper carrying a small dropping funnel is inserted into the flask so that the bottom of the funnel dips into the test-tube. The flask is then exhausted to a pressure of 50 mm. or less, and the outlet closed with a screw clamp. An excess of N -hydrochloric acid, usually about 5 c.c., is admitted slowly from the funnel. When the rapid evolution of carbon dioxide has ceased, the solutions are both agitated by a rotary motion for three minutes. In the case of most substances, this period is sufficient for the complete transfer of carbon dioxide from the inner tube to the barium hydroxide solution. In the analysis of unashed animal tissues, a longer time is necessary, and in the case of bones, at least two hours should be allowed, the solutions being stirred by rotation occasionally during this period and continuously for three minutes at the end of it.

When the reaction is completed, the vacuum is released, the barium carbonate filtered off, and the filtrate titrated with $N/10$ -hydrochloric acid, using phenolphthalein as indicator.

The method appears to be applicable to all carbonates, soluble or insoluble, in the absence of acids, such as hydrogen sulphide, which are highly volatile from aqueous solution. H. W. B.

A Physico-chemical Method of Estimating Alkali Carbonates in the Presence of Alkali Hydroxides. Application to the Analysis of Flue Gases. RENÉ DUBRISAY, TRIPIER, and TOQUET (*Compt. rend.*, 1919, **168**, 56—59).—If 50 c.c. of various solutions, having the same alkalinity, but containing varying proportions of sodium hydroxide and sodium carbonate, are mixed with 50 grams of phenol, heated until solution is complete, and then allowed to cool, it is found that the temperature at which the solution first becomes turbid is higher as the proportion of sodium carbonate to sodium hydroxide increases. The authors have plotted curves for solutions having, respectively, a total alkalinity of $2N$, N , $N/2$, and $N/4$, showing the relationship of temperature to sodium carbonate present. By means of these, the amount of sodium carbonate in a given solution containing both carbonate and hydroxide may readily be determined by bringing the total alkalinity up to one of the four strengths given above by addition of sodium hydroxide, then proceeding as described above and reading off the amount of sodium carbonate present from the curve.

For the determination of the amount of carbon dioxide present in flue gases, 1 litre of the gas is bubbled through 71.5 c.c. of

N/4-sodium hydroxide, and then the above estimation is carried out on the resulting liquid, the amount of carbon dioxide present in the flue gases being readily calculated from the amount of sodium carbonate found in the solution. W. G.

Estimation of Alkali Hydroxide and Alkali Carbonate in Alkali Hypochlorite Solution. M. PHILIBERT (*J. Pharm. Chim.*, 1918, [vii], **18**, 260—272).—The total alkalinity is found by treating a portion of the sample with a measured excess of *N*/10-hydrochloric acid and potassium iodide solution, titrating the liberated iodine with thiosulphate solution, then adding potassium iodide-iodate solution, and again titrating the iodine with thio-sulphate solution; the latter titration is a measure of the quantity of the added acid which remains uncombined, and the difference corresponds with the alkalinity of the sample. To estimate the free alkali hydroxide, another portion of the solution is treated with a measured quantity of *N*/10-barium hydroxide solution, barium chloride solution is also added, the mixture diluted to a definite volume, filtered, and the alkalinity of the filtrate titrated as described above. The difference between the quantities of free and total alkali gives the amount of alkali carbonate. [See, further, *J. Soc. Chem. Ind.*, 1919, February.] W. P. S.

Carnot's Method for the Estimation of Potassium Salts. CAROLINA ETILE SPEGAZZINI (*Anal. Soc. Quim. Argentina*, 1918, **6**, 196—209).—Analyses according to the original prescription of Carnot (this Journal, 1877, ii, 921) gave results in every case much too high. The same method as modified by Grandeau and by Fresenius also gave high results.

It is essential in the preparation of the bismuth chloride solution from the subnitrate to give particular attention to the acidity and temperature of the resulting solution, the optimum acidity being determined by precipitation of a known quantity of potassium from *N*/10-solution.

Good results were obtained only with pure dilute solutions of potassium chloride (*N*/10—*N*/1). Nitrate solutions also gave good results, but with sulphate solutions the results were much too low.

With mixtures of potassium chloride and calcium chloride, magnesium chloride, or sodium chloride, the method is satisfactory only when the potassium salt is in excess. W. S. M.

Method for the Estimation of Potassium in Blood. S. W. CLAUSEN (*J. Biol. Chem.*, 1918, **36**, 479—484).—Two c.c. of plasma or 1 c.c. of blood are oxidised by boiling with 5 c.c. of a mixture of sulphuric and nitric acids (1:20) for half an hour. The excess of nitric acid is quickly evaporated, and the residual liquid washed into a beaker, rendered alkaline, and then evaporated to dryness. The residue is taken up in glacial acetic acid and the potassium precipitated by sodium cobaltinitrite. The precipitate is collected and then heated with dilute sodium hydroxide, which

changes all the nitrite groups to sodium and potassium nitrite, whilst the cobalt is precipitated as the insoluble hydroxide. The nitrites are then estimated by acidifying with sulphuric acid and titrating with permanganate at 70°.

The method appears to give accurate results.

H. W. B.

Gravimetric Analysis. VIII. Separation of Calcium from Magnesium. L. W. WINKLER (*Zeitsch. angew. Chem.*, 1918, **31**, 214—216).—The following method was found to be the most trustworthy for the separation of calcium and magnesium. The neutral solution, measuring 100 c.c. and containing not more than 0.1 gram of calcium and 0.05 gram of magnesium, is treated with 3 grams of ammonium chloride and 10 c.c. of *N*/1-acetic acid, then boiled, and 20 c.c. of 2.5% ammonium oxalate solution are added slowly. The precipitated calcium oxalate is collected after twenty-four hours, dried at 100°, and weighed. The magnesium in the filtrate is precipitated and weighed as ammonium magnesium phosphate (compare A., 1918, ii, 455).

W. P. S.

Volumetric Estimation of Barium. THOS. STEEL (*Analyst*, 1919, **44**, 29).—In the method proposed by Waddell (A., 1918, ii, 407), the use of water saturated with barium chromate is recommended for washing the precipitate of barium chromate. [See, further, *J. Soc. Chem. Ind.*, 1919, February.]

W. P. S.

Estimation of Copper by Means of Potassium Thiocyanate, Potassium Iodide, and Thiosulphate. I. M. KOLTHOFF (*Chem. Zeit.*, 1918, **42**, 609—610).—The process as described by Bruhns is criticised, and modifications are suggested; trustworthy results are obtained if the copper solution is acidified with sulphuric acid after the potassium iodide has been added. The method may be used for estimating the excess of copper in sugar estimations and for estimating copper in the presence of iron, provided that sodium pyrophosphate is added to inhibit the action of ferric salts. [See, further, *J. Soc. Chem. Ind.*, 1919, February.]

W. P. S.

Estimation of Copper and Sugar. G. BRUHNS (*Zeitsch. angew. Chem.*, 1918, **31**, 246).—A reply to Schoorl and Kolthoff's modification of the method described originally by the author (A., 1918, ii, 276).

W. P. S.

A Very Exact and Rapid Method for the Estimation of Mercury in the Majority of its Compounds. S. PINA DE RUBIES (*Anal. Fis. Quim.*, 1918, **16**, 661—689).—The method proposed is a combination of the method of Rose-Finkener and that of Eschka, combining the accuracy of the former with the rapidity of the latter. A critical discussion of both methods with the modifications introduced by Cumming and Macleod, and Biewend and Holloway, is given, together with a bibliography of recent literature on the subject since 1914.

The new method as applied to the analysis of mercury minerals

is as follows. The mineral is mixed intimately with fine iron powder, and is carefully heated in a porcelain crucible into which is closely fitted as a cover a small crucible of gold or silver for the condensation of the volatilised mercury. The cooling of the upper crucible is effected by means of a small bladder of indiarubber which, when distended by a steam of cold water, is in close contact with the whole interior surface. After cooling, the inner crucible is washed with alcohol, and the weight of the condensed mercury film determined. The results obtained by this procedure showed a maximum error of 0.07%.

In the case of more volatile compounds of mercury, organic and inorganic, anhydrous potassium carbonate and barium peroxide, either separately or mixed, are substituted for the iron powder.

When the substance to be analysed contains much moisture, for example, a solution, a weighed quantity is evaporated to dryness in the porcelain crucible after the addition of sodium sulphide, and the mercury is determined as before.

The method is applicable without special modification to the analysis of mercury fulminate and fulminate mixtures.

W. S. M.

Analysis of Aluminium Alloys. A. TRAVERS (*Chim. et Ind.*, 1918, **1**, 708—711).—The alloy is heated with sodium hydroxide solution containing a small quantity of sodium carbonate, and the mixture is filtered. The filtrate contains the zinc and aluminium; the zinc is precipitated as sulphide and estimated acidimetrically after precipitation as ammonium zinc phosphate, whilst the aluminium is estimated by Stock's method. The insoluble portion of the alloy is then dissolved in nitric acid, the solution boiled with the addition of ammonium persulphate, the iron and manganese precipitated with ammonia, the precipitate then dissolved in hydrochloric acid, and the iron titrated with titanium trichloride solution; manganese is estimated in a separate portion of the alloy by the persulphate method. If cobalt and nickel are present, they must be separated as sulphides before the manganese is estimated; cobalt is precipitated by means of β -nitrosonaphthol. The magnesium is estimated in the filtrate from the iron and manganese precipitates, and copper is estimated iodometrically in a separate portion of the sample. [See, further, *J. Soc. Chem. Ind.*, 1919, February.]

W. P. S.

Analysis of Aluminium Alloys and Metallic Aluminium. J. J. FOX, E. W. SKELTON, and F. R. ENNOS (*J. Soc. Chem. Ind.*, 1918, **37**, 328—333T).—A detailed description is given of methods suitable for the separation of lead, manganese, silicon, copper, tin, iron, zinc, magnesium, and nickel in aluminium and in aluminium alloys containing a low or high proportion of zinc.

W. P. S.

Estimation of Molybdenum in Ferromolybdenum. W. HOEPFNER and O. BINDER (*Chem. Zeit.*, 1918, **42**, 564).—A weighed quantity of about 0.5 gram of the sample is heated with

nitric acid (D 1.2), sulphuric acid is then added, and the heating continued until sulphuric acid fumes are evolved; the solution is diluted to 250 c.c., heated with the addition of a few drops of nitric acid, and the iron precipitated with ammonia. The precipitate is dissolved in sulphuric acid and reprecipitated. The two filtrates, which now contain all the molybdenum, are mixed, treated with 50 c.c. of ammonium sulphide, then acidified with sulphuric acid, and heated. The precipitated molybdenum sulphide is collected and weighed, or it may be converted into molybdic acid by ignition. Traces of impurities may be separated by dissolving the molybdic acid in ammonia. Copper, if present, may be separated as described previously (A., 1918, ii, 372).

W. P. S.

The Precipitation of Zirconium Phosphate. GEORGE STEIGER (*J. Washington Acad. Sci.*, 1918, 8, 637—639).—In estimating zirconium in minerals by precipitation as phosphate, the composition of the precipitate approximates more closely to that of normal zirconium phosphate as the acidity of the solution increases. The presence of as much free sulphuric acid as possible is advisable to prevent simultaneous precipitation of iron and titanium phosphates, whilst thorough oxidation with hydrogen peroxide is also necessary to prevent titanium precipitating. At least 3%, and possibly as much as 5%, of free sulphuric acid may be present without interfering with the accuracy of the results. Other phosphates, with the exception of those of the rare earth metals, are readily soluble in the acid solution, and may be separated from the filtrate. [See also *J. Soc. Chem. Ind.*, 1919, February.]

C. A. M.

Analysis of Commercial "Pure" Benzols. F. BUTLER JONES (*J. Soc. Chem. Ind.*, 1918, 37, 324—327 π).—In a mixture containing benzene, thiophen, toluene, carbon disulphide, and "paraffin," the quantity of carbon disulphide is proportional to the difference between the freezing points of the mixture before and after its removal; similarly, the subsequent removal of the thiophen (by means of basic mercuric sulphate) also results in a difference in the freezing point which is proportional to the amount of substance removed. The residual liquid is a mixture of benzene, toluene, and "paraffin"; the difference between its freezing point and that of pure benzene gives the sum of the amounts of toluene and "paraffin" present; the specific gravity of the liquid in conjunction with the freezing point affords a means of estimating these two constituents. A graph is given for solving the four equations involved.

W. P. S.

Modification of Webster's Test for Trinitrotoluene in Urine. F. TUTIN (*Lancet*, 1918, ii, 554; from *Physiol. Abstr.*, 1918, 3, 452).—The urine is extracted with ether, acidified with mineral acid, and again extracted with ether; in the second extract,

an azoxy-compound from trinitrotoluene gives a violet coloration with alcoholic potassium hydroxide. The modifications now proposed are in part minor ones, such as the number of times extraction is performed, but an important change consists in extracting the final ether extract with dilute sodium carbonate solution; this removes substances which mask the characteristic colour of the Webster reaction.

H. W. B.

Estimation of Small Quantities of Ethyl Ether in Ethyl Alcohol. H. E. Cox (*Analyst*, 1919, **44**, 26—27).—The method depends on the fact that alcohol of 99% and upwards distils unchanged; any ethyl ether present passes over in the first fractions, and a mixture of constant boiling point is not formed. The amount of ethyl ether may therefore be estimated from the specific gravity before and after distillation, the specific gravity of the alcohol being taken as that obtained after removal of the ethyl ether. [See, further, *J. Soc. Chem. Ind.*, 1919, February.]

W. P. S.

The Use of Diastatic Reagents. (II) The Detection of Pyramidone and the Differentiation of the Naphthols.

LUCIANO P. J. PALET (*Anal. Soc. Quim. Argentina*, 1918, **6**, 250—257).—To the solution of pyramidone are added some small pieces of the root of lucerne, which contains oxydases and peroxydases. A violet-blue colour is produced on the root fibres on keeping. The addition of hydrogen peroxide accelerates the appearance of, but does not intensify, the colour. The further addition of α -naphthol immediately produces an intense wine-red colour characteristically different from that produced by β -naphthol. This constitutes a delicate test for the presence of small quantities of α -naphthol in β -naphthol.

W. S. M.

Assay and Estimation of Nitroso- β -naphthol. PAUL NICOLARDOT and LUCIEN VALLI-DOUAU (*Bull. Soc. chim.*, 1918, [iv], **23**, 455—459).—For the assay, 2 grams of the material dried at 35° are dissolved in 120 c.c. of acetone in the cold, diluted to 200 c.c. with water, and 100 c.c. of this solution is titrated with a 1.5% solution of iron alum previously standardised against pure nitroso- β -naphthol, the end-point being shown by means of ammonium thiocyanate as an external indicator.

For an exact estimation, an excess of iron alum is added to the solution prepared as above, and the precipitate formed is left overnight, collected, washed free from iron salts with water, dried at 70°, and weighed. It contains 90.7% of nitroso- β -naphthol.

W. G.

Volumetric Estimation of Reducing Sugars. A Simplification of Scales's Method for Titrating the Reduced Copper without Removing it from the Residual Copper Solution. W. BLAIR CLARK (*J. Amer. Chem. Soc.*, 1918, **40**, 1759—1772. Compare A., 1916, ii, 117).—The principle of the

method here described is as follows. The sugar solution to be analysed is boiled under standard conditions with a copper citrate-carbonate solution, and the cuprous oxide dissolved by means of hydrochloric acid. Standard iodine solution is then added to oxidise the cuprous salt, and the excess of iodine titrated by means of sodium thiosulphate. To obtain consistent results, it is necessary to carry out the whole operation under exactly standard conditions. These conditions and the strengths of solutions to be used are indicated for quantities of reducing sugar up to 0.075 gram. It is essential, however, for the worker to standardise his own conditions. The sugar factor of the sodium thiosulphate must be determined on a known sample of reducing sugar, using approximately the same quantity as that to be determined and the same conditions of reduction. The ratio of copper to reducing sugar is approximately constant, the greatest variation occurring with small quantities of sugar.

It was found that sucrose in quantities not exceeding 100 mg. per 10 c.c. and 50% ethyl alcohol do not reduce copper citrate-carbonate solution, but 10% formaldehyde effects a small reduction. [See also *J. Soc. Chem. Ind.*, 1919, February.] E. H. R.

Source of Error in the Use of Picric Acid in Colorimetric Estimations in Biological Fluids. ALICE ROHDE and MARION SWEENEY (*J. Biol. Chem.*, 1918, **36**, 475—477).—It is shown that picric acid which has been preserved in a moist condition for several months loses some of its power of precipitating chromogenic substances in the blood. The use of such picric acid for the estimation of dextrose in the blood by the Benedict-Lewis colorimetric method would yield too high values. H. W. B.

The Colorimetric Estimation of Sugar in the Blood by the Reduction of Picric Acid. C. SALOMON (*Biochem. Zeitsch.*, 1918, **90**, 39—52).—As a result of the critical examination of the method of Lewis and Benedict and its modifications, the author arrives at the conclusion that it has considerable value as regards accuracy and speed for clinical investigations. S. B. S.

Estimation of Dextrose in the Blood. F. HAMEL (*Bull. Sci. Pharmacol.*, 1918, **25**, 223—224; from *Chem. Zentr.*, 1918, ii, 769).—Ten c.c. of venous blood are treated with 10 c.c. of a 10% solution of trichloroacetic acid, and, after removal of the precipitated protein, the dextrose is estimated by Fehling's solution in the usual way. H. W. B.

Estimation of Sugar in Milk and Urine. B. SJOLLEMA (*Chem. Weekblad*, 1918, **15**, 1483—1485).—The method of Folin and Denis (*A.*, 1918, ii, 208) for estimating sugar in milk and urine is recommended. A. J. W.

Estimation of Lactose. E. HILDT (*Compt. rend.*, 1918, **167**, 756—759).—For the determination of lactose in milk in which

the sugar has undergone more or less hydrolysis, the author recommends completing the hydrolysis by means of sulphonic acids, such as those of benzene or phenol or those described by Twitchell (A., 1900, ii, 296), and determining the cupric reducing power. One % solutions of these acids hydrolyse 0.5% solutions of pure lactose in four hours at 100°, but milk serum requires longer heating. No destruction of galactose occurs as when mineral acids are employed. In the determination of reducing power, using 10 c.c. of boiling alkaline copper solution, 0.0506 gram of hydrolysed lactose is equivalent in reducing power to 0.0708 gram of lactose hydrate or 0.0495 gram of invert-sugar.

Considerable destruction of sugar takes place when the solids of milk which has become unsound are dried at 100°; this is attributed to the formation of melanoidins (see Maillard, A., 1912, i, 169) by interaction of sugar and proteolytic products. [See, further, *J. Soc. Chem. Ind.*, 1919, 51A.] J. H. L.

Micro-estimation of Lipoids by Titration. IVAR BANG (*Biochem. Zeitsch.*, 1918, **91**, 86—103).—The fats are oxidised by *N*/10-potassium chromate solution at the ordinary temperature in presence of excess of sulphuric acid. Excess of chromate solution is then estimated by the addition of potassium iodide and the titration of the liberated iodine by thiosulphate solution. The fat (from blood, etc.) is taken up in benzene solution, a little alkali is added (to emulsify the fat), and then the solvent is distilled off. Cholesterol can be estimated in the same manner (and the same factor is used in making the calculations; this factor is determined empirically, as under the conditions of experiment employed, the oxidation is not complete). When cholesterol is present with fats, the determination of both constituents can be made by precipitation of the cholesterol as digitonide, which is insoluble in benzene. When cholesterol esters are present with fats, the determination of the amounts of the constituents can be made in two ways. Either a strength of alkali can be employed which will hydrolyse the fats, but not the cholesterol ester, which can then be separated from the soaps by benzene, or sufficient alkali can be added to saponify both fats and cholesterol esters, and the cholesterol can then be extracted by benzene and estimated separately. In another portion, fats and esters can be estimated together by oxidation. A series of experiments on the oxidation of the lecithides is also described. S. B. S.

The Micro-estimation of the Lipoids of the Blood. IVAR BANG (*Biochem. Zeitsch.*, 1918, **91**, 235—256).—An amplification of the author's micro method (preceding abstract) is given. Cholesterol and neutral fats are extracted first by a fraction of light petroleum of low boiling point containing chiefly pentane. These can be separated by the method already given, using the digitonin compound of cholesterol. After extraction with petroleum, the blood is extracted with 92% alcohol in the cold. This fraction contains the phosphatide and the cholesterol esters. S. B. S.

Gravimetric Estimation of Glycyrrhizin. A. ASTRUC and (MLLE.) G. PICHARD (*J. Pharm. Chim.*, 1918, [vii], **18**, 289—290).—Three grams of dry liquorice extract are dissolved in 30 c.c. of water containing five drops of ammonia, the solution is filtered, and 20 c.c. of the filtrate are treated with 2.5 c.c. of sulphuric acid; the precipitated glycyrrhizic acid is collected after twenty-four hours, washed with 30 c.c. of water, then dissolved in ammonia, and the solution evaporated. The residue is dried at 100° and weighed; to the weight obtained is added 0.04 gram as a correction for the solubility of the glycyrrhizic acid in the wash-water. [See, further, *J. Soc. Chem. Ind.*, 1919, February.]

W. P. S.

A New and Delicate Reaction of Pyramidone and its Differentiation from Antipyrine. LUCIANO P. J. PALET (*Anal. Soc. Quim. Argentina*, 1918, **6**, 151—155).—The author finds that an acid solution of pyramidone when treated with a few drops of an acid solution of potassium ferricyanide and ferric chloride gives an intense blue coloration and precipitate of Prussian-blue. The test is very delicate. With antipyrine, a blood-red colour is obtained with the same reagent. This colour is converted into a pale yellow by the addition of a few drops of hydrochloric acid. The test is therefore carried out in hydrochloric solution, which permits the blue due to the presence of pyramidone in a mixture to emerge. In this way, 1/100 part of pyramidone may be detected in one part of antipyrine.

Phenacetin, acetanilide, aspirin, exalgin, and caffeine give no reaction with the reagent.

W. S. M.

The Reaction of the "Ferri-ferric" Reagent with Alkaloids, Glucosides, and other Vegetable Principles. LUCIANO P. J. PALET (*Anal. Soc. Quim. Argentina*, 1918, **6**, 156—158).—An extension of the application of a mixed solution of potassium ferricyanide and ferric chloride as a reagent (see preceding abstract) to the characterisation of alkaloids, glucosides, and other substances of vegetable origin.

Of 102 substances of this kind tested, 42 gave a positive reaction, that is, a more or less intense blue coloration.

W. S. M.

Estimation of Phenacetin and other *p*-Aminophenol Derivatives by Means of Hypochlorous Acid. A. D. POWELL (*Analyst*, 1919, **44**, 22—25).—For the estimation of *p*-aminophenol, *p*-phenetidine, etc., the substance is treated with hydrochloric acid and sodium hypochlorite solution, the excess of chlorine is removed by a current of air, potassium iodide is then added, and the liberated iodine titrated with thiosulphate solution. In the first phase of the reaction, *p*-benzoquinonechlorimine is formed; this, after the removal of the excess of chlorine, reacts with hydriodic acid, liberating four atoms of iodine, *p*-aminophenol being re-formed. In the case of phenacetin, a preliminary boiling for two hours with hydrochloric acid is necessary. Each c.c. of *N*/10-thiosulphate

solution is equivalent to 0.00273 gram of *p*-aminophenol, 0.00343 gram of *p*-phenetidine, or 0.00448 gram of phenacetin. [See, further, *J. Soc. Chem. Ind.*, 1919, February.] W. P. S.

Arsenotungstic and Arsenotungstomolybdic Complexes as Reagents for Phenolic Amines. LUIS GUGLIEMELLI (*Anal. Soc. Quim. Argentina*, 1918, **6**, 185—195).—Reagents prepared by boiling solutions of sodium tungstate with arsenic acid, and a mixture of sodium tungstate and molybdate with arsenic acid, until concentrated hydrochloric acid no longer produces a precipitate, have been shown to give delicate colour reactions with phenols and some purine derivatives. The same reaction, that is, an intense blue colour, is given by phenolic amines. The author has investigated a large number of substances of this class, and also nitro-, sulphonic and hydroxy-derivatives of these. Positive results were given with the first reagent with the substances $\text{NH}_2\cdot\text{OH}$, $\text{NH}_2\text{--NH}_2$, NHR--NH_2 , NHR--NHR , NHR--OH , and also with compounds containing the same groups separated from each other, but united directly to a benzene, naphthalene, purine, or pyrazolone nucleus. The second reagent reacts with substances containing the same groups, and, in addition, with substances containing one amino-group, for example, aniline. W. S. M.

Estimation of the Carbamide Fraction in Blood. HEINRICH SCHUR and FRANZ URBAN (*Wien. Klin. Wochenschr.*, 1918, **31**, 892—896; from *Chem. Zentr.*, 1918, ii, 673).—The blood serum is freed from albumin by treatment with sulphosalicylic acid solution (20%); nitrogen is estimated by means of bromine and sodium hydroxide in accordance with the method of Knop and Hüfner. H. W.

Detection of Quinine. HANS SALOMON (*Ber. deut. pharm. Ges.*, 1918, **28**, 273—275).—The green coloration obtained when a quinine solution is treated with chlorine and then with ammonia will detect 1 part of quinine in 10,000. The fluorescence observed when a quinine solution is treated with dilute sulphuric acid will detect 1 part of the alkaloid in 200,000 parts. It is advantageous to use bromine-water in place of chlorine in the above test, since it is easier to add just the requisite quantity; the bromine is added until the solution is coloured slightly yellow. Another sensitive reagent for quinine consists of potassium iodide (10 grams), mercuric chloride (2.7 grams), water (200 grams), and glacial acetic acid (2.5 grams). [See, further, *J. Soc. Chem. Ind.*, 1919, 54A.] W. P. S.

Estimation of Quinine in Animal Tissues. W. RAMSDEN, I. J. LIPKIN, and E. WHITLEY (*Ann. Trop. Med. Parasitol.*, 1918, **12**, 233—258).—See this vol., i, 106.

Estimation of Morphine in Complex Products. I. Revision of the Analytical Reactions Involved. ALFRED TINGLE (*Amer. J. Pharm.*, 1918, **90**, 689—706).—A discussion of

various methods and reactions used in the estimation of morphine; the acidimetric method and iodometric method (depending on the formation of the periodide) are trustworthy, but the iodoacidimetric method cannot be used. In methods where the morphine is precipitated by ammonia, the presence of alcohol should be avoided. Barium hydroxide solution does not dissolve morphine completely in the presence of lead acetate. The statement in the British Pharmacopœia that morphine tartrate gives the reactions of morphine and of tartrates is substantially correct. [See, further, *J. Soc. Chem. Ind.*, 1919, 27A.] W. P. S.

Estimation of Morphine in Complex Products. II. Mixtures containing Morphine as a Simple Salt. ALFRED TINGLE (*Amer. J. Pharm.*, 1918, **90**, 788—795).—The following method is described for the estimation of morphine in powders, pills, etc., provided that the alkaloid is not present in the form of opium. Six grams of the sample are warmed with 2 grams of calcium carbonate and 20 c.c. of water until disintegrated, 60 c.c. of cold saturated barium hydroxide solution are then added, the mixture is shaken, diluted to 100 c.c., and filtered. Fifty c.c. of the filtrate are treated with dilute sulphuric acid in quantity just sufficient to precipitate the barium, the mixture then diluted to 55 c.c., and filtered. Fifty c.c. of this filtrate are neutralised with sodium hydroxide solution, then rendered slightly acid with hydrochloric acid, evaporated to 5 c.c., and extracted five times with a mixture of chloroform and alcohol (2:1) after the solution has been rendered alkaline by the addition of a slight excess of saturated sodium hydrogen carbonate solution; 25 c.c. of the solvent are used each time. The residue obtained on evaporating the solvent from the extract is titrated with *N*/10-sulphuric acid, using cochineal or lacmoid as indicator. [See, further, *J. Soc. Chem. Ind.*, 1919, 54A.] W. P. S.

Estimation of Tyrosine in Proteins. CARL O. JOHNS and D. BREESE JONES (*J. Biol. Chem.*, 1918, **36**, 319—322).—Tyrosine can be estimated in a protein after hydrolysis with hydrochloric acid by means of the colorimetric method of Folin and Denis (*A.*, 1912, ii, 1012). Tryptophan and hydroxytryptophan are destroyed during the hydrolysis, and their decomposition products, as well as oxyproline, do not give any colour with the Folin-Denis reagent. H. W. B.

New Contact Test for Albumin in Urine. U. P. STEWART (*J. Amer. Med. Assoc.*, 1918, **71**, 1050; from *Physiol. Abstr.*, 1918, **3**, 451).—The reagent is an aqueous solution of picric acid, magnesium sulphate, and citric acid. H. W. B.

General and Physical Chemistry.

Quantitative Spectra of Lithium, Rubidium, Cæsium, and Gold. A. G. G. LEONARD and P. WHELAN (*Sci. Proc. Roy. Dubl. Soc.*, 1918, **15**, 274—278).—The spark spectra of dilute solutions of the chlorides of lithium, rubidium, cæsium, and gold have been photographed with the object of ascertaining the persistency and intensity of the lines with dilution. The measurements were made with a single prism quartz spectrograph (Hilger). In the case of lithium chloride, the most persistent lines are $\lambda\lambda$ 6708.2 and 4602.5; these lines persist to a dilution 0.001%, whilst the line λ 6103.8 only persists to 0.01%. The lines of rubidium chloride do not exhibit any remarkable persistency, only one, λ 4571.8, appearing with a 0.1% solution. Solutions of cæsium chloride exhibit a fair number of lines, the most persistent being $\lambda\lambda$ 4593.5, 4555.5, 4540.2, and 2525.8, these all being visible in a 0.001% solution. The solution lines of gold chloride are not very persistent; no lines are visible in a 0.01% solution; the lines obtained from a 0.1% solution are $\lambda\lambda$ 4792.8, 4310.7, 3927.8, 3133.2, 3122.9, 2918.5, 2676.1, 2641.6, and 2201.4. J. F. S.

Gamma Ray Activity of Thorium-D. HERBERT N. MCCOY and G. H. CARTLEDGE (*J. Amer. Chem. Soc.*, 1919, **41**, 50—53. See this vol., ii, 120).—Two methods are described for the determination of the γ -ray activity of thorium-D. The first consists in measuring the activity of the sulphide in terms of a standard (0.355 mg. radium) and making emanation determinations by the method previously described (*loc. cit.*). The second method consists in sealing radiothorium precipitate in a crystallising dish and comparing with radium in a similar dish. As a mean value of the experiments, it is shown that $\text{Th-D}:\text{Th}=0.956 \times 10^{-7}$. Using the value found by McCoy and Henderson (*A.*, 1918, ii, 422), that 1 gram of radium is equivalent to 8.85×10^6 grams of thorium, it is shown that 1.46×10^{-7} grams of radium has the same γ -activity as 1 gram of thorium. Combining the $\text{Ms}:\text{Th}$ ratio 0.52×10^{-7} with the present $\text{Th-D}:\text{Th}$ ratio, the value 1.48×10^{-7} is the radium equivalent of the γ -products of thorium determined separately. Thorium-D therefore furnishes 1.81 times as much γ -activity as the mesothorium in equilibrium with the same amount of thorium. Taking account of the fact that only 35% of the thorium disintegrates into thorium-D, this means that, atom for atom, thorium-D contributes 5.17 times as much γ -activity as mesothorium. J. F. S.

Absorption of X-Rays. TYCHO E:SON AUREN (*Phil. Mag.*, 1919, [vi], **37**, 165—207).—Making use of the method previously described (*A.*, 1917, ii, 350), the author has determined the relative

absorption coefficients of a number of elements, including aluminium, iron, nickel, copper, and tin, and of a very large number of inorganic and organic compounds. In the case of the compounds, the additive law has been found valid throughout. With the possible exception of carbon, the state of aggregation appears to have no influence on the amount of adsorption. In examining chemical compounds in which the same element appears, but with differing valencies, it is shown that there is no difference in the quantity of absorption in any case. The relation between the atomic absorption coefficients for most elements has been determined at the medium wave-lengths $\lambda = 0.38, 0.36, 0.34,$ and 0.30×10^{-8} cm. Assuming that absorption for hydrogen is exclusively due to scattering produced by the electron combined with the atomic nucleus, it has been found likely that scattering for other elements is solely due to the electrons constituting the outer layer of the respective atoms, that is, to the "outer electrons," and by aid of the relative atomic absorption coefficient for hydrogen, the number of the outer electrons has been estimated for the lighter elements. The atomic absorption coefficient increases for different elements by groups nearly proportionally to the atomic number. If it is accepted that the atomic number gives the number of electrons combined with the atomic nucleus, it is possible from the increase of absorption with increasing atomic number to determine the distribution of electrons between the outer and inner regions. From Barkla and White's determinations of the ratio μ/ρ for copper and water, a formula of the mass scattering coefficient for different elements has been deduced. The values calculated for the relative absorption coefficients for γ -rays agree fairly with the observed absorption coefficients. The value of the mass scattering coefficient of aluminium for γ -radiation, calculated by means of the above-mentioned formula, agrees very nearly with the value directly observed by Ishino. The number of the outer electrons in the lighter elements seems to be the same for the elements placed in the same group of the periodic system, and the distribution of electrons thus appears to be in close connexion with the periodicity of the chemical qualities of the elements as expressed by this system.

J. F. S.

Investigation of Röntgen Spectra. *M*-Series. W. STENSTRÖM (*Ann. Physik*, 1918, [iv], **57**, 347—375).—The author has investigated the *M*-series of Röntgen spectra for the elements uranium, thorium, bismuth, lead, thallium, gold, platinum, iridium, osmium, tungsten, tantalum, lutecium, ytterbium, erbium, holmium, and dysprosium. It is shown that the older method of measuring Röntgen spectra is not suitable for the soft radiations of the *M*-series, but that better results are obtained if a glowing cathode and high-frequency transformed alternating current are used. As cathode, a Wehnelt cathode was at first employed, but this was later replaced by a tungsten spiral. To find a grating of suitable constant, many crystals were examined and the constant

determined. These included rock salt, $d = 2.814 \times 10^{-8}$ cm.; potassium chloride, $d = 3.136 \times 10^{-8}$ cm.; calcite, 3.028×10^{-8} cm.; gypsum, 7.621×10^{-8} cm.; potassium ferrocyanide, 8.454×10^{-8} cm.; mica, 10.1×10^{-8} cm.; quartz, 4.23×10^{-8} cm.; beryl, 4.61×10^{-8} cm. (on plane 0.0.0.1) and 8.06×10^{-8} cm. (on plane 1.0.1.0); sodium ammonium tartrate, 7.30×10^{-8} cm.; sucrose, 10.56×10^{-8} cm.; and the compound, $\text{AgNaC}_6\text{H}_8\text{O}_4\text{S}_2, \text{Na}_2\text{C}_6\text{H}_8\text{O}_4\text{S}_2, 10\text{H}_2\text{O}$, $d = 19 \times 10^{-8}$ cm. From a discussion of the sources of error, it is shown that the probable error of the measurements does not exceed 0.2—0.3%. The present measurements were made with a gypsum crystal, and it is shown that, in addition to the α - and β -lines, a γ -line also exists in the M -series, and this conforms to the Moseley relationship. Other lines appear in some cases, but these are in all probability due to impurities. Each of the main lines is diffuse and wide, and the blackening decreases with decreasing wave-length. They consist of several single lines, which were not sufficiently separated for characterisation.

J. F. S.

Conductivity. IV. Conductivity of Alkaline Earth Formates in Anhydrous Formic Acid. H. I. SCHLESINGER and R. D. MULLINIX (*J. Amer. Chem. Soc.*, 1919, **41**, 72—75. Compare A., 1912, ii, 26; 1914, ii, 703; 1916, ii, 210).—The electrical conductivity of solutions of calcium formate and strontium formate has been determined in anhydrous formic acid solutions at 25°. The conductivity concentration curves are composed of three parts—of two straight lines which intersect at about $N/10$, and a portion which curves upward in a manner similar to that observed for sodium formate (*loc. cit.*). It is likely that these salts ionise into a metal formate ion, which in more dilute solutions is decomposed into a simple metal ion, and that this second ionisation becomes sufficiently great at the concentrations where the two curves meet to affect the conductivity appreciably.

J. F. S.

Depolarisers of the Becquerel Effect. ALEXANDER VON SAMSONOW (*Zeitsch. wiss. Photochem.*, 1918, **18**, 141—176).—Working with oxidised copper electrodes, the author has studied the action of certain depolarisers on the electrode when immersed in solutions of sodium sulphate, bromate, iodate, and chlorate. The potential rises much higher in iodate and bromate solutions than in sulphate and chlorate solutions. As depolarisers, ferrous sulphate, glycine developer, sodium sulphite, iron oxalate, *p*-amino-phenol, sodium arsenite, and sodium phosphite were used. Working hypotheses of the Becquerel effect and the action of the depolarisers are discussed.

J. F. S.

Phenomenon of Electrical Supertension. A. SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 375—381. Compare this vol., ii, 8).—A theoretical paper in which an unattackable electrode is considered as a hydrogen electrode from the point of

view of the phase rule. The supertension of electrodes is considered from the same point of view, and a $\Delta-x$ diagram is drawn to illustrate the process. It is shown that there is no essential difference between the phenomena of supertension and polarisation. The former is only a little more complicated in so far that here an unattackable electrode has been inserted into the system. When, however, the phenomenon of supertension is considered at attackable electrodes, the process becomes identical with that of polarisation.

J. F. S.

Periodic Passivity of Iron. II. A. SMITS and C. A. LOBRY DE BRUYN (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 382—385. Compare A., 1917, ii, 262).—A continuation of previous work in which it was shown that anodically polarised iron could be activated by the introduction of halogen ions. Hence, by the electrolysis of a solution of ferrous sulphate and ferrous chloride, the phenomenon of passivity can be made periodic. This periodic property has now been photographically recorded, together with the time duration of each stage of the process. The potential difference varies between -0.3 volt and $+1.4$ volts with respect to the normal calomel electrode, and the current density changed from 33 milliamperes to 28 milliamperes per sq. cm. With a sealed-in electrode 1.5 cm. long, the iron was active for a short period and passive for a comparatively long period. With a smaller current density, the active and passive periods become nearly equal. The effects on the curves produced by changing the relative depth of the electrodes have been studied. Using a larger iron electrode, the potential difference showed irregular oscillations, whilst the current strength was regularly periodic. The irregularity was such that even the most active state did not recur regularly, and the whole curve shows periodicity under the influence of great disturbances. Hence it follows that the electrode was never active throughout the whole area at the same time. This confirms the previous view that the difficulty of rendering iron passive increases with increasing size.

J. F. S.

The Sign of the Electrical Phenomenon and the Influence of Lyotropic Series observed in this Phenomenon. H. ZWAARDEMAKER and H. ZEEHUISEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 417—427. Compare A., 1918, ii, 351).—The nebula produced when an unsaturated solution of salicylic acid is sprayed always possesses a negative electric charge. This charge is weakened by both anions and cations, in the order $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+ < \text{NH}_4^+$ for cations, and $\text{CNS}^-, \text{NO}_3^- < \text{I}^-, \text{Cl}^-, \text{Br}^-, < \text{C}_2\text{H}_3\text{O}_2^- < \text{tartrate ion} < \text{PO}_4^{3-} < \text{citrate ion} < \text{SO}_4^{2-}$ for anions. Acetic acid weakens or completely destroys the negative charge of salicylic acid. In higher concentrations with a positive electrical phase, it prevails as an acid over salicylic acid sprayed in weak solutions, which gives a negative charge. Acetates also have a weakening effect on the charge of salicylic acid, whereas of them-

selves they produce no charge. Mixtures of salicylic and acetic acids showed the electrical property of acetic acid so long as the latter acid is present in the larger quantity. If the concentration of acetic acid in the mixture falls so low that such a solution of acetic acid alone would give scarcely any effect, then the charge of the mixture sinks to zero; in still lower concentrations of acetic acid, the charge reappears, but this time negative. J. F. S.

Dependence of the Magnetic Properties, the Specific Resistance, and the Density of Iron Alloys on their Thermal Treatment. E. GÜMLICH (*Zeitsch. Elektrochem.*, 1918, **24**, 372—377).—The density, specific resistance, temperature coefficient of the resistance, the first and second transition points, and the magnetic properties (coercive force, retentiveness, permeability, and hysteresis loss) have been determined before and after annealing processes carried out under various conditions on pure electrolytic iron, commercial iron (seven specimens), iron alloys with carbon (0—1·8%), with silicon (0—8·5%), with aluminium (0—10·5%), and manganese (0—16%). In the case of pure iron, the following values were obtained: D 7·876; specific resistance per sq. mm., 0·0994; temperature coefficient of the resistance between 20° and 100°, 0·57%; saturation value, $4\pi J_{\infty} = 21,620$, where J is the intensity of magnetisation. These values were very little changed by annealing and stand in contrast to the magnetic properties. It is shown that the improvement in the magnetic properties brought about by annealing is not due, as generally believed, to a molecular change, but rather to the removal of adsorbed gases. In rich carbon alloys, the first and second transition points lie in the same position as those given in the diagram of condition. In the curves between the carbon content and the density, coercivity and saturation value, respectively, there is a sharp break at the point where, normally, cementite separates from perlite or martensite. The carbon content has a marked effect on the coercive force. This quantity increases approximately 7 gauss per 1% increase in the carbon content in the case of perlite and 70 gauss in the case of martensite. With smaller carbon content, the influence is much greater; thus with 0·1% carbon impurity, the coercive force rises 0·7 gauss. The presence of silicon diminishes the magnetic properties; this substance behaves like non-magnetic impurities, which diminish the magnetic properties of the iron. The presence of aluminium affects the iron in much the same way as silicon; the specific resistance increases nearly proportionally to the aluminium content. The second transition point is lowered 100° by 10% of aluminium. The manganese alloys show similarities to the carbon alloys. The coercive force is extraordinarily high after annealing, and with 10% manganese has a value of 60 gauss, whereas the retentiveness disappears with 14—16% manganese. With manganese concentrations 8—9%, the density, specific resistance, and the magnetic properties show great irregularity. The transition points show a marked tempera-

ture hysteresis, and from this it is deduced that alloys containing 10—12% manganese cannot be magnetised. J. F. S.

Diamagnetism in Weak [Magnetic] Fields. O. E. FRIVOLD (*Ann. Physik*, 1918, [iv], **57**, 471—488).—The magnetic susceptibility of tellurium, water, sulphur, antimony, zinc, gold, and silver has been investigated in magnetic fields of varying strength. With the exception of zinc, all the elements investigated show a dependence, with respect to their susceptibility, on the strength of the field for weak fields. In the case of higher field strengths, the susceptibility is constant except in the case of silver. The susceptibility is constant for field strengths down to 100 gauss in the case of zinc, to 600 gauss for gold, to 250 gauss for antimony, to 200 gauss for tellurium, and above 600 gauss for sulphur. Silver is paramagnetic in weak fields, but becomes diamagnetic in fields above 800 gauss. In the case of antimony, tellurium, and sulphur, a very strong dependence on the field strength for weak fields is displayed. The susceptibility of gold shows a dependence on the field strength which is in keeping with the theory of Gauss, and on the basis of this theory, the number of magnetons per cu. cm. has been calculated and the value 1.7×10^{14} obtained. Consequently, a magneton of gold contains 3.65×10^9 atoms.

J. F. S.

The So-called First Quantum Theory of Planck. The Quantum Theory of Paramagnetism. ADOLF SMEKAL (*Ann. Physik*, 1918, [iv], **57**, 376—400).—A theoretical paper in which three formulæ are deduced to represent susceptibility. These formulæ are tested on measurements for ferric sulphate, manganese sulphate, and the tetrahydrate of manganese sulphate, and a comparison is made with the quanten theories of Planck. J. F. S.

Thermal Conductivity of Neon. S. WEBER (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 342—356).—The thermal conductivity of neon has been determined under various pressures by Goldschmidt's method, which consists in electrically heating a wire in the gas and from resistance measurements calculating the rate of conduction. A correction is introduced for loss of heat at the ends of the wire. The thermal conductivity of neon at the following temperatures is shown to be: 105.9° , $k' = 0.0001344$; 0° , 0.0001087 ; -74.37° , 0.0000879 ; and -181.43° , 0.0000499 . These values are compared with the values calculated by means of the formula of Sutherland and a general formula of Maxwell. It is shown that, whilst there is good agreement in the second case, Sutherland's formula appears to be inapplicable at low temperatures. From a comparison of the thermal conductivities of argon, helium, and neon, it appears that the reduced thermal conductivity of neon changes in a different manner with the reduced temperature than the similar values for argon and helium. J. F. S.

Empirical Formula for Calculating the Specific Heat of Water. J. NARBUTT (*Physikal. Zeitsch.*, 1918, **19**, 513—514).—The author has deduced an empirical formula for calculating the specific heat of water over the temperature range 0—100°. This formula is based on the experimental results of Ludin, Dieterici, Bousfield (A., 1911, ii, 580), Callendar (A., 1912, ii, 428), and Barnes and Cooke, and has the form $c_t = 1.00733 - 0.0007416t + 0.000016845t^2 - 0.00000009552t^3$, where $c_{15} = 1$. The agreement between the values calculated by this formula and the best experimental values are extremely good. J. F. S.

Calculation of the Ratio of the Principal Specific Heats of Benzene and cycloHexane by Leduc's Cyclic Method. G. DEJARDIN (*Compt. rend.*, 1919, **168**, 161—164).—Using Leduc's formula (compare *Ann. Physique*, 1915, [viii], **23**, 577), the author finds that the value of γ , the ratio of the principal specific heats, for benzene at 20° is $\gamma = 1.106$ and at 100° $\gamma = 1.116$, and for cyclohexane between 20° and 90° is $\gamma = 1.077$. Using the formula $\gamma = 1 + 2/(\mu + \lambda)$, where μ is the number of degrees of liberty relative to the kinetic energy of the molecule and λ is the intramolecular potential energy, the author finds for benzene $\gamma = 1.111$ and for cyclohexane $\gamma = 1.083$ or 1.074 , according as the degrees of liberty are taken as 24 or 27. W. G.

Thermochemical Studies : Simplified Formula for Calculating the Molecular Latent Heat of Evaporation. DANIEL LAGERLÖF (*J. pr. Chem.*, 1918, [ii], **98**, 136—142).—Since all the author's calculated values and also Thomsen's experimental values for the heats of combustion of the hydrocarbons refer to the gaseous state, whilst most of the experimental values obtained by other authors refer to liquid or solid compounds, comparison of these different values requires a knowledge of the molecular latent heat of evaporation. The latter has been determined in but few cases, and can be derived only from Deprez and Trouton's law, $q/T = \text{constant}$. For the value of this constant, van't Hoff deduced the mean value 20.55 cal., whilst for non-associated liquids Kurbatov obtained the mean value 20.7 cal., the variation from the mean being at most 3—4%. From the equation

$$w_{\text{vap.}} = q = 20.55T$$

(or $20.7T$), the author derives the expressions $q = 0.02t + 5.6 + 0.00055t$ and $q = 0.02t + 5.65 + 0.0007t$, which refer to kilogram calories; $t = T - 273$. In order to arrive at an expression which may be easily remembered, he combines these two equations, with the result: $q = w_{\text{vap.}} = 0.02t + 5.6 + 0.0007t$. The third, variable member of the right-hand side may be neglected for values of t numerically less than 15°. The available experimental data show, however, that for uninuclear, aromatic hydrocarbons a fourth negative member must be introduced, the equation then becoming $w_{\text{vap.}} = 0.02t + 5.6 + 0.0007t - (t - 80^\circ)/300$. It is not known if cor-

rection is needed for multinuclear aromatic hydrocarbons, since no experimental numbers exist.

The values for the different terms of the above equations and the calculated and experimental values of w_{vap} are given in tabular form for a large number of hydrocarbons of different kinds. The differences between the calculated and experimental values are sometimes marked, but in most cases the agreement between them is extremely good.

T. H. P.

Thermochemical Value of the Linkings Uniting the Atoms in Crystals. M. PADOA (*Atti R. Accad. Lincei*, 1918, [v], 27, ii, 327—331).—If the union of the atoms in crystalline networks is affected by means of valency (compare this vol., ii, 51), a relationship should exist between the thermochemical data and the values of such linkings. Since the heat of combustion of diamond is 94.32 Cal. per gram-atom, and $\text{CO} + \text{O} \rightarrow \text{CO}_2 + 68.22$ Cal., and since the thermochemical equivalence of the four valencies of carbon has been demonstrated, the difference $94.32 - 68.22 = 26.10$ Cal. may be taken as the heat of formation of carbon monoxide from an atom of carbon combined in diamond, and the difference $68.22 - 26.10 = 42.12$ as the heat of disintegration of the carbon atom, that is, the heat-equivalent of the energy required to dissolve the linking holding it in the crystal. From the structure of the diamond, it follows that with each carbon atom there correspond four half-valencies or two whole ones, so that each valency has the value $42.12 : 2 = 21.06$ Cal. A similar value is obtained in the case of graphite.

Each free atom of carbon gives, then, on complete combustion, $94.32 + 42.12 = 136.44$ Cal., and four free hydrogen atoms yield similarly four times the heat of combustion of a gram-atom of molecular hydrogen plus twice the heat of dissociation of the hydrogen molecule, that is, $4 \times 34.35 + 2 \times 95 = 327.40$ Cal. Hence the sum $136.44 + 327.40 = 463.84$ Cal., diminished by the observed heat of combustion of methane, namely, 212.70 Cal., gives 251.14 Cal., which constitutes the heat of formation of the methane molecule from its constituent free atoms; consequently, each C-H linking corresponds with $251.14 : 4 = 62.78$ Cal. Similar calculation of the value of the C-C linkings in normal, saturated, open-chain hydrocarbons gives numbers varying from about 16 Cal. for the lower to about 18 Cal. for the higher members of the series.

In the case of benzene, which, according to Thomsen ("Thermochemistry," 1908. 393. 449), behaves thermochemically as if it contained nine simple linkings, and thus corresponds with the centric formula, each of these nine linkings represents a value of 16.6 Cal. With other cyclic hydrocarbons, increase in the number of nuclei is accompanied by increase in the mean number of linkings competing for each carbon atom, this number tending to the limiting value 2; at the same time, the mean value for each C-C linking increases towards the value, 21.0, for graphite. With hydrogenated hydrocarbons, such as cyclohexane, decahydronaphthalene, and *n*-octane,

the C-C values are somewhat higher than with the corresponding non-hydrogenated ones. T. H. P.

The Heat of Dissociation of Diatomic Gases in Relation to the Increase in the Value of \sqrt{a} of the Dissociated Atoms. J. J. VAN LAAR (*Chem. Weekblad*, 1918, 15, 1124—1137).—The theoretical considerations of this paper are based on the regularities observed by the author which are found to exist when the values of b and \sqrt{a} of the van der Waals's equation of state are brought into relation to the groups of the periodic system (A., 1916, ii, 386—387, 610; 1917, ii, 67). The values of b and \sqrt{a} for a compound are shown to be additive properties of the substance calculable from the values of the corresponding constants of the constituent elements. The value of b for any element is found to be independent of its state of combination, whether the element occurs free or combined in a molecule. On the other hand, \sqrt{a} , which is dependent on the mutual attraction of the molecules, is subject to variation according as the atom to which it relates is more or less shielded by other atoms in the molecule. For example, the values of \sqrt{a} for the carbon atom in CH_4 , silicon in SiH_4 , nitrogen in NH_3 , are in each case found to be zero, that is, the central atom exerts no external attraction. In the case of hydrogen, nitrogen, oxygen, and the halogens, all of which dissociate into single atoms in suitable conditions of temperature, it has been found that \sqrt{a} is greatly increased in the monatomic state of the gas. \sqrt{a} thus becomes a measure of the "valency attraction" of the two atoms (\sqrt{A}), whilst the value of \sqrt{a} ordinarily to be attributed to the same atom in compounds represents the "residual attraction." For carbon, the ratio of the two values is 32:3.1. Between the two constants $\sqrt{A_K}$ and $\sqrt{a_K}$ at the critical temperature, the following relation is established:

$$\sqrt{A_K} = \sqrt{a_K} \times \sqrt{\left(1 + \frac{4}{5} \theta Q_0 / T_K\right)},$$

where Q_0 is the energy liberated at $T=0$ in the formation of one gram-molecule of gas from the free atoms, T_K is the critical temperature, and θ a constant approximating to unity. The values of \sqrt{A} for various gases (hydrogen, nitrogen, oxygen, the halogens) calculated from this equation are in satisfactory agreement with the values which correspond with the position of these elements in the periodic arrangement. W. S. M.

The Effect of some Simple Electrolytes on the Temperature of Maximum Density of Water. ROBERT WRIGHT (T., 1919, 115, 119—126).

Compressibility of Aqueous Solutions, especially of Urethane, and the Polymerisation of Water. THEODORE W. RICHARDS and SVEN PALITZSCH (*J. Amer. Chem. Soc.*, 1919, 41, 59—69).—The compressibility of water and of aqueous solu-

tions of urethane has been carried out by the method previously described (A., 1912, ii, 896). The concentration was varied from 0—56.01%, and the compressibility determined for pressures between 100—300 megabars. All experiments were conducted at 20°. In addition to these determinations, the solution volume, the surface tension, and the viscosity of urethane solutions were also determined. It is shown that with rising concentration, the compressibility decreases rapidly from 43.25×10^{-6} (the compressibility of pure water) to 38.91×10^{-6} , the compressibility of a solution of 34 grams of urethane in 100 grams of water. From this point, the compressibility increases, at first slowly and then more rapidly; at the highest measured concentration, 127.35 grams of urethane in 100 grams of water, the compressibility is 40.86×10^{-6} . The surface tension, specific volume, and viscosity showed no such minimum, and it is shown that none is to be expected. The results emphasise the theory of Whiting, which ascribes polymerisation to water.

J. F. S.

Determination of the Compressibility of Solids at High Pressures. LEASON H. ADAMS, ERSKINE D. WILLIAMSON, and JOHN JOHNSTON (*J. Amer. Chem. Soc.*, 1919, **41**, 12—42).—The compressibility of quartz, calcite, aluminium, sodium chloride, lead, brass, cadmium, zinc, tin, silver, copper, gold, bismuth, a tin-bismuth alloy, tool steel, and silica glass has been determined for pressures up to 12,000 megabars. The principle of the method employed is to compare the change of volume under pressure of a cylinder of the material with that of a similar cylinder of soft steel, the compressibility of which was considered to be 0.60×10^{-6} cm.²/megadyne. In carrying out the determination, the solid, surrounded by a liquid such as kerosene, was enclosed in a thick-walled steel bomb fitted with a movable non-leaking piston, and pairs of simultaneous readings were made of (1) the displacement of the piston, that is, the volume change, and (2) the pressure. The piston displacement was measured to 0.01 mm. by means of a dial micrometer. In measuring the pressure, advantage was taken of the change of resistance under pressure of a "therlo" wire, and in order to determine the pressure to within 1 megabar, the resistance was measured with a type of Wheatstone bridge having no movable contacts. The $P\text{-}\Delta v$ graph for gold, copper, brass, silver, aluminium, and calcite, like that of steel, is linear, but the graph for zinc, tin, cadmium, lead, the tin-bismuth alloy, quartz, bismuth, and sodium chloride shows an appreciable curvature, thus indicating for those substances a measurable decrease of compressibility with increasing pressure. A comparison was made of the compressibility of two alloys with that of their components. In the case of a simple mixture, such as the tin-bismuth alloy, the measurements indicate that the compressibility of mixtures the other properties of which, such as specific volume, electrical conductivity, and specific heat, are approximately linear functions of the composition, is related in the same

simple way to the compressibility of the separate components. On the other hand, the compressibility of alloys of the class to which brass belongs is much lower than the sum of the individual compressibilities.

J. F. S.

Thermal Dissociation of Sulphur Dioxide. J. B. FERGUSON (*J. Amer. Chem. Soc.*, 1919, **41**, 69—72. Compare this vol., ii, 15).—Starting from the equilibrium constant of the reaction $\text{CO} + \frac{1}{2}\text{SO}_2 \rightleftharpoons \text{CO}_2 + \frac{1}{2}\text{S}_2$, the author has calculated the degree of dissociation and the equilibrium constants of sulphur dioxide over the temperature range 1000—1500° and at pressures from 1 atm. to 0·001 atm. The degree of dissociation at 1500° and 1 atm. is found to be 5·9, whilst at 0·001 atm. it is 59. Consequently, it is obvious that the dissociation of sulphur dioxide is less than the dissociation of either carbon dioxide or water vapour.

J. F. S.

Capillarity Constants of Pure Mercury and of Liquid Potassium Amalgam in Contact with Potassium Iodide Solutions. V. POLARA (*Atti R. Accad. Lincei*, 1918, [v], **27**, ii, 322—327).—Gouy (A., 1892, 760) showed that the capillarity constant of mercury in contact with aqueous potassium iodide solutions assumes a maximum value somewhat less than that of the same metal in contact with dilute sulphuric acid (1:6 by vol.). This behaviour is in contradiction to Lippmann's law, according to which the capillarity constant should be a function solely of the potential difference at the contact, and its maximum hence independent of the nature of the substances in contact. By means of Quincke's apparatus, the author has investigated the influence of the concentration of the potassium iodide on the maximum value of the capillarity constant of the mercury in contact with it and on the polarisation determining such maximum. Gradual increase of the concentration is found to be accompanied by progressive lowering in the maximum value of the capillarity constant, the difference for the two extreme cases ($N/10$ and $10N$) amounting to a variation of about 1 mm. in the difference of level between the two limbs of the apparatus; within the limits of sensitiveness of the method, the polarisation requisite for obtaining the maximum depression does not appear to be influenced by the concentration. Depression of the surface tension of the solution by addition of ethyl alcohol in various proportions produces marked lowering of the maximum of the capillarity constant, especially for percentages of the alcohol not exceeding 40; for higher proportions of alcohol, the effect is less pronounced. Also, potassium amalgams (2—0·1 part of potassium per 1000 of mercury) in contact with normal potassium iodide solution exhibit a capillarity constant which is somewhat lower than the maximum capillarity constant of pure mercury in contact with sulphuric acid solution, and diminishes sensibly with increase of the proportion of potassium dissolved in the mercury, the diminution being slower for the more concentrated than for the more dilute amalgams.

Study of the variations in the density of the electric double layer at the contact with the polarisation by an apparatus detecting a change of 0.1 volt in the polarisation confirms the relation $X = -dA/dp$, where X is the density of the double layer, A the capillarity constant, and p the polarisation. This relation may be brought into accord with the circumstance that the capillarity constant does not depend solely on the potential difference at the contact by assuming that the function A has the form $A = S - T(V - p)$, where S , the ordinary surface tension, is independent of the potential difference at the contact, but depends, in agreement with the results obtained, on the particular conditions of the contact; $T(V - p)$ is the symbol of a function only of the potential difference $(V - p)$ existing at the contact for each value of the polarisation employed (V = potential difference due to the contact and p the polarisation employed), and satisfying also the conditions $dT/dp = X$ and $(dT/dp)_{p=v} = 0$. T. H. P.

Velocity of Diffusion. PHILIPP FRANK (*Physikal. Zeitsch.*, 1918, 19, 516—520).—A mathematical paper in which formulæ are deduced for the velocity of diffusion of gaseous molecules. The calculations are based on considerations of the Brownian movement, and are made in connexion with single particles and with the rate of advance of the "head" of a particle swarm.

J. F. S.

Crystal Assemblage in Relation to the Atomic Field of the Crystal. R. GROSS (*Jahrb. Radioaktiv. Elektronik.*, 1918, 15, 270—292).—The author uses the term "Sammelkrystallisation" (crystal assemblage) to signify the transformation of a substance from an amorphous or sub-crystalline to a distinctly crystalline state. A number of examples of the phenomenon are discussed. One of the most striking examples is a process used for making tungsten filaments. The finely divided metal, obtained by reduction of the oxide, is pressed into the form of wire and drawn slowly through a small heated coil at a temperature of 2000—2200°. When the rate of passage of the wire through the heated coil is properly regulated, it becomes converted into a single homogeneous, elongated crystal, the rate of growth of the crystal being equal to the rate at which the wire is travelling. The particles of tungsten of which the wire is originally composed have a mean diameter of about 10^{-5} cm., and it has been shown by Debye (A., 1917, ii, 574) by the X-ray method that this powder consists of cubic, crystalline particles. Other examples of crystal assemblage are afforded by the increase in size of the crystals of many metals by annealing, by the formation of silver crystals from a silver sol, and by the formation of calcite crystals when powdered calcium carbonate is heated under pressure. Some substances, for example, calcium sulphate, have a greater solubility than the normal when the particles in equilibrium with the solution are very small in size, but in course of time the solu-

bility falls to the normal owing to increase in the size of the particles. It is shown thermodynamically that the solubility should increase when the particles become very small, and it is concluded that the theory of minimum surface energy does not adequately explain crystal growth, since for very small particles the surface energy is not independent of the size. E. H. R.

Liquid Crystals. II. Melting and Congelation Phenomena with *p*-Azoxyanisole. W. J. H. MOLL and L. S. ORNSTEIN (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 254—258).—In a previous paper on the extinction of liquid crystals, it was suggested that two varieties of liquid crystals of *p*-azoxyanisole exist, ex-solid (produced by melting the solid) and ex-liquid (produced by cooling the isotropic liquid). To confirm this point, the authors have determined the fusion and congelation curves of *p*-azoxyanisole, and show from the results that there is no evidence from this source of the existence of two forms of liquid crystals of *p*-azoxyanisole. On the other hand, these curves show the existence of three solid forms of this substance: *p*-azoxyanisole I (m. p. 118°), *p*-azoxyanisole II (m. p. 104·5°), and *p*-azoxyanisole III (m. p. 116°). A fourth form, which melts at 108°, was shown to exist in the previous paper, but this form did not appear in the present work, and it is now shown only to be capable of existence in capillary layers (between glass). J. F. S.

Molecular Mechanism of Colloidal Behaviour. I. The Swelling of Fibrin in Acids. RICHARD C. TOLMAN and ALLEN E. STEARN (*J. Amer. Chem. Soc.*, 1918, **40**, 264—272).—The amount of swelling of blood fibrin in solutions of hydrochloric, nitric, sulphuric, acetic, and formic acids of various concentrations has been determined, as well as the amount of acid adsorbed by the fibrin from the solution. Similar experiments have been carried out with solutions of sodium chloride and with solutions of the above-named acids to which sodium chloride has been added. The data obtained are in accordance with the authors' theory of the molecular mechanism of protein swelling. This theory embraces the following points. On account of the amphoteric nature of protein colloids, they possess a marked tendency to adsorb hydrogen ions from acid solutions and hydroxyl ions from alkaline solutions. In an acid solution, the adsorbed hydrogen ions, together with an equivalent number of anions, form a "double layer" on the walls of the pockets or pores in the interior of the gel, and this leads to swelling and the imbibition of water by electrostatic repulsion. The addition of a strong electrolyte to such a swollen colloid, either a neutral salt or excess of the strong acid which caused the original swelling, will furnish ions in the interior of the pockets which will tend to arrange themselves so as to neutralise the electrical fields of the adsorbed layers, and thus bring about a reduction of the swelling. The addition of a neutral salt to an acid solution tends to neutralise the electrical field of

the adsorbed acid, and hence makes it easier for more acid to reach the surface of the pockets, thus leading to increased adsorption. Salts with multivalent ions should be more effective in reducing swelling than salts with univalent ions, since, for example, a bivalent ion will take up no more room than a univalent ion and will be twice as effective in neutralising an existing electric field. No assumptions are made as to the molecular nature of the adsorption of the hydrogen or hydroxyl ions; the theory would be equally tenable if the adsorption process should lead to a fairly uniform coating of ions over the whole of the exposed surface, or, on the other hand, if the hydrogen ion should only tend to go on to the protein molecule at special points where there is a particularly strong stray field, for example, where the amino- and acid groups of the amino-acids approach one another. J. F. S.

Colours of Colloids. WILDER D. BANCROFT (*J. physical Chem.*, 1918, **22**, 601—630).—A theoretical paper in which the author discusses the nature of the colour of natural objects. The subject is treated historically, and the various types of colouring individually treated. Colours are divided into two groups: (1) structural colours, and (2) pigmentary colours. The former group of colours owes its existence to the refraction, absorption, and interference of light. J. F. S.

Degree of Dispersion of Colloids and its Determination. GEORGE KING (*J. Soc. Chem. Ind.*, 1919, **38**, 4—7r).—A short account is given of the slit ultra-microscope and its capabilities. In counting the number of colloidal particles in a definite volume of colloidal solution, it is necessary, owing to the rapid Brownian movement, to take the mean of the numbers of particles observed at ten momentary observations, and the solutions should be diluted with colloid-free medium until there are never more than four particles in the field at the same time. The periodic illumination may be effected by allowing a pendulum screen to swing in front of the micrometer slit, the impression of the number of particles seen being then very definite. The solution in the observation cell should be changed at least ten times, and the mean of the one hundred separate counts taken; further, one or more controls with fresh dilution should always be made.

The paraboloid, Leitz, and Cotton and Mouton devices for dark-ground illuminations serve well for qualitative observation, but are useful only for coarse hydrosols; they are, moreover, unsuitable for the rapid examination of colloidal solutions, as the adjustment of the instrument must be disturbed for each small quantity observed and a fresh volume of solution introduced into the special microscope slide. With the cardioid ultra-microscope, it is possible to distinguish particles beyond the range of the old slit ultra-microscope, owing to the fact that the hydrosol can be more intensely illuminated. The slit ultra-microscope has now been enhanced in sensitiveness by using objectives of high numerical

aperture (1.05), one at right angles to the other, the front lenses, made of quartz, being both immersed in the hydrosol. By this means, the size of the particles which can be counted is diminished from 5μ to 3μ , whilst even smaller particles can be seen in concentrated solution, but not accurately counted in dilute solution.

With the new immersion ultra-microscope, qualitative examinations were made of solutions of peptone, starch, gelatin, agar-agar, and dextrin in the concentrations used by Findlay and King (T., 1913, 1170; 1914, 1297), but these were found to be optically clear under the best conditions for illumination, etc.; the refractive indices of the medium and colloid are doubtless nearly equal. Merck's ferric hydroxide is, however, countable.

Of physiological interest is the condition of casein in cow's milk and human milk. The particles in the latter are uncountable in the slit ultra-microscope, but they can be counted in the new instrument, whilst casein in cow's milk is easily seen in the slit ultra-microscope. Thus it would seem that, when it is to be used for feeding infants, cow's milk should be so treated as to cause an increase in the degree of dispersion of the casein particles; this is not effected by mere dilution of the milk.

When it is necessary to determine the size of microscopic particles in a suspension, use may be made of Stokes's formula, $V = F/6\pi\eta r$, where V = velocity of fall, F = force acting, η = viscosity, and r = radius of particle. Other methods which have been used are discussed by Henri (*Trans. Faraday Soc.*, 1918, 47), but are not convenient for technical application. T. H. P.

The System Iron-Oxygen. A. SMITS and J. M. BLIJVOET (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 386—400).—A theoretical paper in which the three-phase systems FeO, Fe, gas and $\text{Fe}_3\text{O}_4, \text{FeO, gas}$ are considered. The gas in question is either of the reducing mixtures CO_2, CO , or $\text{H}_2\text{O, H}$. On the basis of the deductions drawn from the above-mentioned considerations, the processes operative in the blast furnace are theoretically investigated. The $P.T.$ diagram of the system oxygen-iron is derived from the equilibria of the iron oxides in reducing and oxidising gases respectively. Calculations are made of the oxygen dissociation tension, and these values, as was to be expected, are very small. J. F. S.

Influence of Temperature on Homogeneous Gas Reactions. GEORGE W. TODD and S. P. OWEN (*Phil. Mag.*, 1919, [vi], **37**, 224—230).—A mathematical paper in which from Maxwell's distribution theorem an expression has been deduced by which the number of molecules having a velocity greater than a particular value may be calculated. This expression has the form

$$n = 2Ne^{-x^2} / \sqrt{\pi}(x_1 + \frac{1}{2}x_1),$$

in which n is the number of molecules per c.c. which have a velocity greater than c , and $x = c\sqrt{m/2R\theta}$; all the other factors have their usual significance. Assuming that only molecules with kinetic

energies greater than a definite minimum have the power to react with other molecules, it is shown how the velocity constant of a gaseous reaction varies with temperature. This is represented for the general case by the equation

$$k_{\theta_2}/k_{\theta_1} = \phi\theta_2/\phi\theta_1(e^{w(1/\theta_1 - 1/\theta_2)}),$$

in which W is a constant. The general relationship for the dependence of the equilibrium constant on the temperature is also deduced.

J. F. S.

The Evolution and Magnetic Properties of Chromic Hydroxide in Alkaline Solution. F. BOURION and A. SENECHAL (*Compt. rend.*, 1919, **168**, 89—91. Compare this vol., ii, 66).—The velocity constants for the rate of oxidation of chromic hydroxide in alkaline solution by hydrogen peroxide at 17° and 30° during the first eight hours correspond fairly well with those for a quadrimolecular reaction. The paramagnetism of an alkaline solution of chromic hydroxide diminishes slowly with time, but the diminution is small and never exceeds 20%.

W. G.

Polar and Non-polar Valency. RAJENDRALAL DE (T., 1919, **115**, 127—134).

Automatic Variation of Gas Pressure and its Application to a Vacuum Pump, Circulation of Gases [and] Magnetic Stirrer. O. MAASS (*J. Amer. Chem. Soc.*, 1919, **41**, 53—59).—An apparatus is described which, when attached to a Toepler mercury pump, may be used for the periodic variation of gas pressure. By suitable adjustments, which are described in the paper, the apparatus may be employed for the circulation of gases and for working a magnetic stirrer.

J. F. S.

Inorganic Chemistry.

Determination of the Rate of Solution of Atmospheric Nitrogen and Oxygen by Water. I. W. E. ADENEY and H. G. BECKER (*Sci. Proc. Roy. Dubl. Soc.*, 1918, **15**, 385—404). —The rate of solution of nitrogen and oxygen in distilled water, tap-water, and sea-water has been determined at temperatures between 11.3° and 12.3° by allowing a bubble of the air to pass up a narrow glass tube containing the water. This affects the mixing of the solution and constantly exposes the air to a fresh surface of water. The object of the experiments was to substantiate the authors' views on the mechanism of solution of a gas in the liquid. Contrary to the generally accepted view, it is held that the gas is

absorbed by the surface layer, but the gases do not remain concentrated here; they are gravitationally drawn downwards through the lower layers of water with comparative rapidity (compare *ibid.*, 1914). J. F. S.

Flame Reactions: Selenium and Tellurium in the Hydrogen-Air Flame. JACOB PAPISH (*J. physical Chem.*, 1918, 22, 640—646).—The elements selenium and tellurium, as well as their dioxides and hydrides, have been introduced into the hydrogen air flame and the colour changes observed. At the same time, experiments were made to ascertain the nature of the deposit, if any, on a cold object introduced into the flame. Selenium dioxide produces a deep blue luminescence in the inner zone, pale blue in the middle zone, and green in the outer zone. There was a deposition of selenium in the inner and middle zones, but no deposition in the outer zone. Hydrogen selenide produces a very faint blue luminescence in the inner zone, deep blue in the middle zone, and green in the outer zone. There was a deposition of selenium in the inner zone, but no deposition elsewhere. Selenium produces a luminescence coloured blue, violet, and green in the inner, middle, and outer zones respectively; in this case and in all following cases, the element was deposited in the inner and middle zones, but there was no deposition in the outer zone. Tellurium dioxide, hydrogen telluride, and tellurium all produce a lilac luminescence in the middle zone and a green luminescence in the outer zone, whilst tellurium dioxide and the free element produce a green luminescence in the inner zone, whereas the hydrogen telluride produces a blue luminescence in this region. Possible explanations for the differences in the various cases are suggested. J. F. S.

The Constitution of Nitrous Vapours. P. JOLIBOIS and A. SANFOURCHE (*Compt. rend.*, 1919, 168, 235—237).—When nitric oxide and oxygen are mixed at the ordinary temperature in the proportion of 4:1 by volume, combination is instantaneous, and nitrogen trioxide is formed and remains unchanged. If the gases are mixed in the proportion of 2:1, or if an excess of oxygen is used, the combination rapidly reaches the stage of the trioxide, but after twenty seconds 34% of the peroxide is formed, after thirty-seven seconds 68%, and after 100 seconds 92%. If nitrous vapours are heated at 400°, the equilibrium tends towards the formation of the trioxide, with partial destruction of the nitrous vapours. W. G.

The Synthesis of Ammonia at High Temperatures. III. EDWARD BRADFORD MAXTED (T., 1919, 115, 113—119).

Production of Ammonia from "Nitrolime," and the Time Yield under Various Conditions. WERNER GRAHMANN (*Zeitsch. Elektrochem.*, 1918, 24, 385—391).—The rate of produc-

tion of ammonia from boiling mixtures of "nitrolime" and water, "nitrolime" and sodium hydroxide or sodium carbonate of various concentrations, and "nitrolime" and potassium hydroxide or carbonate of various concentrations has been determined. In the case of "nitrolime" and water, it is shown that the rate of decomposition of calcium cyanamide is extremely slow in all concentrations at the boiling point and atmospheric pressure. Thus a 1% solution is decomposed to the extent of 98% by seventy-two hours' boiling. In the presence of sodium carbonate, the decomposition really amounts to the decomposition of sodium cyanamide (*a*) under a constant sodium hydroxide concentration, and (*b*) under a concentration of sodium hydroxide, which increases during the reaction. In the case of an addition of sodium hydroxide, the decomposition takes place under a regularly increasing concentration of the hydroxide. The same remarks apply to the decompositions in the presence of potassium carbonate and hydroxide. The presence of alkali hydroxide or alkali carbonate has an accelerating influence on the reaction; the velocity increases with increasing concentration of the added salt to a maximum, after which it remains more or less constant. The maximum in the case of alkali hydroxides occurs with much lower initial concentration of alkali than in the case of the alkali carbonates, for in these experiments the alkali concentration increases continuously from beginning to end of the decomposition. The experiments with potassium hydroxide and carbonate do not show the same maximum as the sodium compounds under similar conditions, so that, since sodium hydroxide and potassium hydroxide are ionised to practically the same extent, it must be taken that the acceleration of the decomposition velocity is not dependent entirely on the hydroxyl-ion concentration, but that the cation and the undissociated molecules also exert a specific action. A number of orientating experiments were carried out under 30 atmospheres pressure at 150°. Under these conditions, it is shown that, even without the addition of alkali, the decomposition takes place very rapidly until 75% of the calcium cyanamide is decomposed, after which the velocity becomes much less, thus: in an aqueous solution 75% is decomposed in forty-five minutes, but only 90% is decomposed in 120 minutes. In the presence of 10% alkali hydroxide, 75% decomposition is reached in thirty minutes and 90% in seventy-five minutes. The "nitrolime" used in the experiments contained 16.85% of cyanamide nitrogen, 0.65% of dicyanodiamide nitrogen, 22.30% free lime, and 0.31% sulphur.

J. F. S.

Effect of Phosphine and Hydrogen Sulphide on the Oxidation of Ammonia to Nitric Acid. GUY B. TAYLOR and JULIAN H. CAPPS (*J. Ind. Eng. Chem.*, 1919, **11**, 27—28).—Pure acetylene has no effect on the catalytic oxidation of ammonia to nitric acid in presence of platinum (compare A., 1918, ii, 265), the opposite results obtained earlier being due to the fact that the acetylene used contained small proportions of phosphine.

Hydrogen sulphide in low concentrations has no immediate toxic effect on the catalytic oxidation. [See *J. Soc. Chem. Ind.*, March.]
T. H. P.

Oxidation of Coal. J. R. PARTINGTON (*Chem. News*, 1919, 118, 50—51).—The experimental results obtained by Wheeler (T., 1918, 113, 945) are discussed, and an alternative explanation offered. The assumption that air is absorbed by freshly won coal with formation of an additive compound, such as a complex oxide, is an improbable one. The facts agree better with the hypothesis that the process is one of adsorption, followed by direct formation of carbon monoxide. Carbon dioxide may be produced by oxidation of the carbon monoxide by moisture, or even by interaction of carbon and water, hydrogen being formed at the same time. The adsorption hypothesis explains the differences observed when moist or dry air is used. In absence of moisture, the proportion of carbon dioxide formed would be expected to be lower than when moisture is present. The fall of the ratio CO_2/CO with rise of temperature also follows from the adsorption hypothesis.
E. H. R.

The Interaction of Stannous and Arsenious Chlorides.
REGINALD GRAHAM DURRANT (T., 1919, 115, 134—143).

Stable Solution of Silver Nitrate. F. LIEBERT (*Chem. Weekblad*, 1919, 16, 74).—The solution of the salt is exposed to the light until the organic matter present is exhausted, and is then filtered through asbestos. The resulting solution may be kept in light without further alteration.
W. S. M.

Atomic Weight of Lead from Samarskite. ARTHUR L. DAVIS (*J. Physical Chem.*, 1918, 22, 631—639).—Using a specimen of lead obtained from samarskite which contained U_3O_8 12.21% and ThO_2 1.03%, the author has determined the atomic weight of this element. The method adopted was that of Baxter and Grover (A., 1915, ii, 456), and consisted in converting lead chloride into silver chloride. In three experiments, results varying from 206.246 to 206.363 were obtained for the atomic weight of lead. Calculations made from the content of samarskite on thorium and uranium lead to a value of 206.06 for the lead contained in this mineral, whereas the experimental value is 206.30. This corresponds with a mixture of 3 parts of radio-lead and 1 part of ordinary lead. If it is assumed that 8% of the uranium is transformed along the actinium series to form a stable isotope of atomic weight 210, the value 206.38 is calculated for the atomic weight of samarskite lead. The experimental value, however, is in better agreement with the supposition that either or both of the isotopes of lead in the thorium series are relatively short-lived, and that the lead in samarskite represents a mixture of radio-lead of the uranium series, atomic weight 206, and radiolead of the actinium

series, atomic weight 210. This conclusion is not in agreement with the value 206.04 found by Hönigschmidt for the atomic weight of lead from crystallised uraninite (A., 1914, ii, 653).

J. F. S.

The Sub-acetate and Sub-sulphate of Lead. HENRY GEORGE DENHAM (T., 1919, 115, 109—113).

The Rusting of Iron on Contact with other Metals and Alloys. O. BAUER and O. VOGEL (*Mitt. k. Materialsprüf.*, 1918, 36, 114—208).—A discussion of previous work and new experiments on the influence of other metals on the corrosion of iron in conductivity water, distilled water, and chiefly 1% sodium chloride solution. Much attention is paid to the potential difference between the metals and electrolyte, which was measured as follows: the cell, together with a millivoltmeter and a resistance of 100,000 ohms, is placed in parallel with a standard resistance, W . A small current, i , is passed, which is adjusted until no deflection of the galvanometer is obtained, when the potential difference = iW . A large number of results are given for the potential difference of pure metals and graphite against the normal calomel electrode. The contact of two metals in the 1% salt solution results in a large increase in the corrosion of the more electro-negative metal, that of the more electro-positive one being reduced. In the water this effect is much less marked. Rusting of iron is entirely prevented when a current was passed which counterbalanced the solution pressure in the electrolyte, so rendering the passage of the ions into solution impossible. For electrolytic iron in 1% sodium chloride solution at 18°, a minimum current density of 0.0000106 amps. per sq. cm. is required, calculated from the formula $(a \cdot F) / (Fe/2 \cdot qs)$, where a is the loss of weight of the iron in grams, F 96,540 coulombs, $Fe/2$ half the atomic weight of iron, q surface of iron in sq. cm. exposed to attack, and s duration of corrosion in seconds. [See, further, *J. Soc. Chem. Ind.*, March.]

F. C. TH.

Investigation of the Crystal Structure of White and Grey Tin by means of X-Rays. A. J. BIJL and N. H. KOLKMEIJER (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, 21, 405—408).—The structure of the two allotropic modifications of tin has been investigated by means of X-rays. The method adopted was that due to Debye and Scherrer, and the interference photographs obtained indicate that both forms of the metal are crystalline.

J. F. S.

Reduction of Osmium Tetroxide by Hydrogen Chloride. OTTO RUFF and SUSANNE MUGDAN (*J. pr. Chem.*, 1918, [ii], 98, 143—144).—The conclusion drawn by Milbauer (A., 1918, ii, 202) that osmium tetroxide is reduced to osmium monoxide by hydrochloric acid is opposed to the results obtained by Ruff and Bornemann (A., 1910, ii, 305) and by Ruff and Rathsburg (A., 1917,

ii, 323), and repetition of Milbauer's experiments by the authors shows that the tetroxide undergoes reduction to a slight extent to the dioxide, but not to the monoxide; the bulk of the tetroxide remains unchanged in the hydrochloric acid solution. Milbauer's erroneous results appear to be due to the presence in the tetroxide of impurities, although the commonest of these, namely, ruthenium tetroxide, behaves similarly to osmium tetroxide. T. H. P.

Mineralogical Chemistry.

Fibrous Quartz from Rhode Island. ALFRED C. HAWKINS (*Amer. Min.*, 1918, **3**, 149—151).—Fibrous quartz resembling asbestos in appearance, and consisting of long, delicate, flexible fibres, fills narrow veins in metamorphic slates at several localities in Rhode Island. It ranges in colour from pure white to green. The green colour is due to the presence of admixed actinolite, as shown by microscopical examination and by the following analyses: I, green from Fenner's Ledge, Cranston; II, white from the same locality; III, green from Portsmouth.

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.	H ₂ O.	CO ₂ .	S.	Total.
I.	77.15	8.72	7.68	0.70	3.96	1.40	—	0.52	100.13
II.	94.92	4.56		trace	trace	0.16	—	—	99.64
III.	91.83	1.61	3.81	0.80	1.37	0.70	0.50	0.12	100.74

L. J. S.

Hambergite from Kashmir. R. C. BURTON (*Rec. Geol. Survey India*, 1913, **43**, 168—172).—Crystals of hambergite, together with cookeite, prehnite, tourmaline, beryl, euclase (?), and amblygonite, have been found in the granitic débris in the Kashmir sapphire mines. They were probably derived from the neighbouring pegmatites. A description is given of a twinned crystal. Analysis gave:

GIO.	B ₂ O ₃ .	H ₂ O.	Total.	Sp. gr.
52.40	[37.39]	10.21	100.00	2.36

L. J. S.

Phosphorite from the Island of Juan de Nova, Madagascar. J. ORCEL (*Bull. Soc. franc. Min.*, 1918, **41**, 104—108).—The phosphate deposits on the small island of Juan de Nova, or St. Christophe, about eighty miles off the west coast of Madagascar, have been formed by the action of soluble phosphates, derived from guano, on the underlying coral-rock. Analysis I is of brown, concretionary phosphorite, and II of brown, earthy material of prac-

tically the same composition. The latter is worked under the name "leached guano." The analysis (I) shows an excess of 8.45% CaO, indicating the voelckerite formula $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaO}$ (A., 1912, ii, 565).

	CaO.	SrO.	MgO.	Al ₂ O ₃ .	P ₂ O ₅ .	Cl.	SO ₃ .
I.	48.63	0.17	1.75	0.15	35.56	0.29	0.56
II.	46.85		n.d.	0.38	35.19	0.14	0.58
	CO ₂ .	Organic matter.	H ₂ O.	Loss at 110°.	Insol.	Total.	
I.	0.14	1.27	7.97	4.00	0.05	100.54	
II.	10.08			5.32	0.03	98.57	

L. J. S.

The Colour Change in Vivianite. THOMAS L. WATSON (*Amer. Min.*, 1918, **3**, 159–161).—The large, pale green crystals of vivianite from Plant City, Florida (A., 1918, ii, 119), are non-pleochroic and yield a colourless powder. This powder rapidly changes, especially in sunlight, to deep blue, and becomes strongly pleochroic. An unground sample of the crystals showed FeO 42.88%, whilst the finely ground material gave FeO 38.43%. The change in colour and pleochroism is thus due to the partial oxidation of the iron, and not to inversion as was at first suggested by the microscopical aspect of the material. A tabulation of the refractive indices of pale green and of dark blue vivianite from various localities indicates that the oxidation has been accompanied by an increase in the values of β and γ .

L. J. S.

Copiapite in Coal. WILLIAM J. MCCAUGHEY (*Amer. Min.*, 1918, **3**, 162–163).—A specimen of pale green, fibrous melanterite from the Congo coal mine in Perry County, Ohio, changed in the course of a year to dull white, and the fibres became brittle. Yellow spots also developed, especially at the points of contact between the melanterite and the associated shale. This yellow material consists of minute, tabular crystals, and is proved by the following analysis and refractive indices to be copiapite, $\text{Fe}_2\text{O}_3 \cdot 5\text{SO}_3 \cdot 18\text{H}_2\text{O}$.

SO ₃ .	Fe ₂ O ₃ .	H ₂ O.	Insol.	Total.	α .	β .	γ .
39.68	29.98	30.45	0.31	100.42	1.525	1.545	1.595

L. J. S.

Nasonite from Långban, Sweden. G. AMINOFF (*Geol. Förh. Förh.*, 1916, **38**, 473).—This mineral, hitherto known only from Franklin, New Jersey (A., 1900, ii, 89), has been observed at Långban in the veins of "secondary calcite," where it is associated with schefferite, native lead, apophyllite, etc. It forms white to pearl-grey lamellar masses, or, less often, hexagonal prisms with

rounded faces. Refractive indices (Na), $\omega=1.9453$, $\epsilon=1.9710$. Analysis by R. MAUZELIUS agrees with the usual formula $\text{Pb}_4(\text{PbCl})_2\text{Ca}_4(\text{Si}_2\text{O}_7)_3$.

SiO_2 .	PbO .	FeO .	MnO .	CaO .	MgO .	Cl .	H_2O .	Total.
18.23	67.67	0.04	0.14	11.29	0.20	2.90	0.24	100.71

L. J. S.

Anorthite from Japan. S. Kôzu (*Sci. Rep. Tôhoku Imp. Univ.*, 1914, Geol. Ser., **2**, 7—33).—The results are given of elaborate determinations of the optical constants (refractive indices, optic axial angle, and dispersion of the optic axes) for different wavelengths of anorthite from three Japanese localities. As these show certain differences amongst themselves, the following analyses, by H. S. WASHINGTON, were made of I, anorthite crystals from Miyake-jima, one of the Seven Izu Islands south of Tokyo, and II, crystals from the Tarumae volcano in Hokkaidô.

SiO_2 .	Al_2O_3 .	Fe_2O_3 .	CaO .	MgO .	K_2O .	Na_2O .	Total.	Sp. gr.
I. 44.49	36.00	0.08	19.49	0.04	0.03	0.59	100.72	2.758
II. 44.03	35.93	0.10	18.66	trace	0.07	1.00	100.24	2.757

Barium and strontium are absent, and the slight differences in composition cannot be correlated with the differences in the optical constants. I corresponds with $\text{Ab}_{3.9}\text{An}_{95.4}\text{Cg}_{0.7}$ and II with $\text{Ab}_{4.7}\text{An}_{92.6}\text{Cg}_{2.0}\text{Or}_{0.6}$. The melting points are 1538° and $1536^\circ \pm 2^\circ$ respectively.

L. J. S.

Racewinite, a New Mineral from Utah. A. N. WINCHELL (*Econ. Geol.*, 1918, **13**, 611—615).—The mineral occurs as veins and irregular masses in limestone, and also replacing the carbonate portion of calcareous sandstones, near the contact with porphyry in the Highland Boy mine at Bingham, Utah, where it is often intergrown with pyrites and other ore minerals. It is brownish-black with a dull to bright lustre, and somewhat resembles coal in appearance. When freshly taken from the mine, it is bluish-green; the change in colour to brownish-black takes place slowly throughout the whole mass, and after six months the largest pieces were altered to the centre. The mineral undergoes other remarkable changes in colour. In boiling nitric acid it is insoluble, but gradually changes to yellowish-brown and translucent. In hydrochloric acid, it is slowly soluble and shows the same change in colour. Thin splinters and particles under the microscope are pale to brownish-yellow. In clove-oil this colour changes first to grass-green and then to black, but the same change does not take place in cedar-oil and some other oils. The finely powdered mineral is nearly white with a yellow tinge. The material is coarsely crystalline with no cleavage or crystal-faces; it is friable and the fracture conchoidal. Sp. gr. 1.94 — 1.98 , H $2\frac{1}{2}$; optically biaxial with large angle and negative, n about 1.51 . It adheres to the tongue and slakes in water, breaking up with a sharp, audible

sound. Analyses I and II by J. P. HICKEY and C. L. AUSTIN respectively:

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.	H ₂ O.	Total.
I.	43.92	23.68	7.37	2.52	0.50	22.04	100.03
II.	43.24	23.69	8.05	2.42	0.78	21.80	99.98

A sample of the green, unaltered mineral showed 0.60% FeO. Over sulphuric acid, 7—8% H₂O is lost in one day and 14% after forty-nine days; this is re-absorbed from a moist atmosphere. Other determinations gave the loss at 70° as 8% and at 200° as 12.1%. Heated to dull redness, the crystal structure is not destroyed, and the optical characters are not materially altered.

L. J. S.

New Swedish Minerals. GUST. FLINK (*Geol. Förh.*, 1917, 39, 426—452).—*Ektropite* forms crusts of small, brown, rectangular plates on garnet with calcite and barytes in magnetite ore from the Norrbotten mine at Långban. The crystals are monoclinic ($a:b:c=0.74:1:0.84$, $\beta=61^{\circ}5'$) with a tabular habit parallel to the orthopinacoid and elongated in the direction of the axis of symmetry. They are opaque with a vitreous to silky lustre, but in thin splinters under the microscope, the material is translucent and yellow. D 2.46, H 4, n 1.62—1.63. Analysis I, by N. SAHLBOM, gives the formula $12\text{RO}, 8\text{SiO}_2, 7\text{H}_2\text{O}$. The mineral is related to carypillite and neotocite.

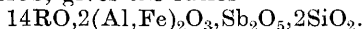
	SiO ₂ .	Sb ₂ O ₅ .	PbO.	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.
I.	35.02	—	—	0.75	—	5.80
II.	7.75	20.76	—	9.50	3.58	2.44
III.	34.72	—	41.74	—	—	—

	MnO.	CaO.	MgO.	H ₂ O.	Total.
I.	37.20	3.59	7.20	8.89	99.89*
II.	52.61	0.58	3.06	0.11	100.39
III.	2.17	20.28	0.20	0.10	99.90†

* Including K₂O 1.13, Na₂O 0.12, metallic sulphides 0.19.

† Including BaO 0.69.

Katoptrite occurs as tabular crystals and irregular lumps with magnetite in granular limestone in the Brattfors mine at Nordmark. The crystals are monoclinic ($a:b:c=0.79223:1:0.48985$, $\beta=78^{\circ}57'$) and have a highly perfect cleavage parallel to the orthopinacoid $a(100)$. This cleavage resembles that of mica, but the cleavage flakes are very brittle and not flexible. D 4.5, H $5\frac{1}{2}$. The mineral is black and opaque with a bright metallic lustre. Thin flakes are red by transmitted light and strongly pleochroic. Analysis II, by R. MAUZELIUS, gives the ratios



The mineral resembles manganostibite in appearance, and it may perhaps be identical with the incompletely described hematostibite.

Margarosanite (A., 1916, ii, 532).—This new mineral has been found in some quantity in the "Lukas Ort" and Bjelkes shaft at Långban, where it is associated with nasonite, schefferite, apo-

phyllite, calcite, etc. The masses, weighing up to 1 kilo., are snow-white with pearly lustre and columnar structure. Crystals are rare; these are triclinic ($a:b:c=0.74998:1:1.2849$, $\alpha=74^{\circ}37'$, $\beta=50^{\circ}28'$, $\gamma=78^{\circ}53'$) with three cleavages, that in one direction being highly perfect. D 4.39, H $2\frac{1}{2}$. Analysis III, by R. MAUZELIUS, gives the formula $\text{PbCa}_2(\text{SiO}_3)_3$. The mineral is readily and completely soluble in dilute nitric acid. It is perhaps a member of the pyroxene group.

Thaumasite from Langban is described as loose aggregates of small but distinct crystals. These are hexagonal with prismatic habit, $a:c=1:0.9479$.
L. J. S.

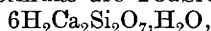
Minerals in the Crystalline Limestone of Crestmore, California. ARTHUR S. EAKLE (*Bull. Dep. Geol. Univ. California*, 1917, **10**, 327—360).—At Crestmore, in Riverside County, two hills of crystalline limestone, resting on a boss of granodiorite and intruded by veins of quartz-monzonite-porphyry and pegmatite, are extensively quarried for the manufacture of Portland cement, the partly decomposed granodiorite (anal. I) being used as a substitute for clay. In one hill the limestone is a white marble (anal. II), whilst in the other it is composed largely of blue calcite. In the latter, the metamorphic processes have been more intense, there having also been hydrothermal action by phosphatic, siliceous, and carbonated solutions, and zones composed of a great variety of metamorphic minerals have been developed at the contacts with the intrusive veins. The blue calcite, which forms bands and patches intermixed with the metamorphic minerals, is sometimes of a deep colour, fading on exposure to sky-blue. It is decolorised at a low heat, and the colour is thus perhaps due to organic matter. Detailed descriptions are given of about fifty mineral species from this locality, and analyses of the following. Wilkeite (A., 1914, ii, 283) and xanthophyllite (A., 1916, ii, 443) have been previously described.

Brucite (anal. III) forms grey, yellow, or red granules embedded in the white limestone. It consists of an aggregate of twisted plates and threads much compressed and strained, and has no doubt been derived from periclase (MgO) with an accompanying considerable ($2\frac{1}{2}$ times) increase in volume. Wollastonite is of abundant occurrence as columnar and fibrous masses; as snow-white, finely granular and loosely coherent aggregates (anal. IV); and as crystals of various types (anal. V of clear crystals). The distribution of the faces on these crystals indicates that the symmetry is monoclinic-hemimorphic, or perhaps triclinic. Several new crystal-forms are noted. The mineral is strongly triboluminescent. Refractive indices, $\alpha=1.614$, $\beta=1.629$, $\gamma=1.631$. Idocrase as yellow or brown crystals and masses is also abundant; anal. VI, by J. B. WRIGHT, of green idocrase. Garnet, crystals and massive, of a cinnamon colour occurs with the idocrase; anal. VII by J. B. WRIGHT, of massive grossularite. A new analysis (VIII by

G. SURR) is given of the monticellite which occurs in intimate association with the xanthophyllite.

Two new species, *crestmoreite* and *riversideite*, hydrated calcium silicates, are described. *Crestmoreite* is an alteration product of wilkeite, and in the description of this mineral it was provisionally referred to as *okenite* (A., 1914, ii, 283). It occurs as small patches of earthy to compact, snow-white, and opaque material in the blue calcite. Under the microscope, it shows straight extinction with positive elongation, low birefringence, and $\beta=1.590$. Hardness 3. It is readily soluble in acid with separation of some flocculent silica, although most of the silica goes into solution. Boiling water extracts some calcium. Water is expelled mostly at a high temperature; at 200° the loss is 3.27%, and at 300° 10.27%. From the analyses IXa—c, a complex formula is deduced, but the phosphate, sulphate, and carbonate no doubt represent admixed unaltered wilkeite. Simpler formulæ are $\text{CaSiO}_3 \cdot \text{H}_2\text{O}$ and $4\text{H}_2\text{CaSiO}_4 \cdot 2\text{H}_2\text{O}$, preference being apparently given to the former.

Riversideite occurs as narrow seams of white, fibrous material in massive idocrase. $\text{H}=3$; refractive indices, $\alpha=1.595$, $\gamma=1.603$; the fibres give straight extinction with positive elongation. A complex formula is deduced from anal. X; neglecting phosphate and sulphate, simpler formulæ are $2\text{CaSiO}_3 \cdot \text{H}_2\text{O}$ and



preference being given to the former. These two new minerals may be regarded as hydro-wollastonites.

Orthoclase, pure white material from the pegmatite, anal. XI. Okenite (anal. XII, by W. FOSHAG) occurs as tufts of long, slender needles and fibres on apophyllite, which is found in cavities in wollastonite between the pegmatites and the limestone. The crystals are probably orthorhombic, $n=1.55$. Prehnite occurs in cavities in the felspar of the pegmatites; in addition to the usual green drusy type, there is also a pale brown to colourless type, which forms crystals or, more often, compact, granular masses. Anal. XIII of the brown prehnite. Laumontite (anal. XIV) as columnar and fibrous masses occurs on the green prehnite.

	SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	P_2O_5	SO_3	CO_2	H_2O	Total	Sp. gr.
I.	60.60	16.61	5.03	—	7.93	2.08	—	—	4.79	—	97.08*	—
II.	4.15	—	1.20	—	50.78	2.50	—	—	40.60	—	99.58	—
III.	—	—	0.55	—	—	67.48	—	—	31.73	—	99.76	2.39
IV.	51.77	—	2.12	—	44.85	—	—	—	1.02	—	99.76	—
V.	50.42	—	0.51	—	48.29	0.60	—	—	0.07	—	99.89	—
VI.	36.88	17.61	3.11	0.46	33.27	4.73	—	—	0.61	—	99.57†	3.36
VII.	35.53	21.11	3.95	0.60	36.06	0.78	—	—	1.23	—	100.15‡	3.39
VIII.	37.46	—	—	2.94	35.14	25.32	—	—	—	—	100.86	3.078
IXa.	36.12	—	—	—	42.71	—	2.38	2.42	1.16	14.98	99.77	—
IXb.	38.30	—	—	—	41.20	—	3.50	1.25	—	15.17	99.42	—
IXc.	34.42	—	—	—	43.54	—	3.50	2.24	—	16.24	99.42	—
X.	41.26	—	—	—	44.58	—	3.84	1.84	—	8.11	99.65	—
XI.	64.54	20.86	trace	—	1.66	trace	—	—	—	0.52	100.81	2.54
XII.	56.17	—	—	—	26.10	—	—	—	—	16.83	99.10	2.206
XIII.	44.10	24.20	—	—	25.20	—	—	—	—	5.86	99.36	—
XIV.	53.49	22.01	—	—	10.80	trace	—	—	—	13.39	99.69	—

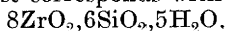
* Alkalis not determined. † Incl. MnO 1.50, CuO 1.06, Na_2O 0.61.

‡ Incl. CuO 0.70, Na_2O 0.20. § Incl. K_2O 11.85, Na_2O 1.18.

L. J. S.

Two New Zircon Minerals—Orvillite and Oliveiraite.

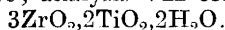
T. H. LEE (*Amer. J. Sci.*, 1919, [iv], **47**, 126—132; *Revista da Sociedade Brasileira de Ciencias, Rio de Janeiro*, 1917, No. 1, 31—38).—The zirconia-bearing rock or ore ("*caldasite*") of the Caldas region in Minas Geraes, Brazil, consists at times mainly of baddeleyite, containing ZrO_2 92%. One variety, in which the cavities are lined with small crystals of zircon, consists of a mixture of zircon and a new zirconium silicate, the latter being soluble in a mixture of hydrofluoric and hydrochloric acids. Analyses I and II are of the mixture, and III of material picked out under the microscope. The last corresponds with the formula



and for this the name *orvillite* is proposed.

	ZrO_2 .	SiO_2 .	TiO_2 .	Al_2O_3 .	Fe_2O_3 .	FeO .	H_2O .	Total.
I.	71.88	25.31	0.62	0.15	—	0.43	1.56	99.95
II.	85.01	9.63	1.52	—	3.57	—	—	99.73
III.	68.04	25.45	—	—	—	—	6.35	99.72

The second mineral—*oliveiraite*—occurs with euxenite (anal. IV) at Pomba, Minas Geraes. Most of the euxenite crystals are coated with a yellow crust (anal. V). An analysis (VI) is also given of another euxenite, from Espirito Santo, which was supposed to contain a new element. The oliveiraite is greenish-yellow with a radially fibrous structure; analysis VII corresponds with



	Ta_2O_5 .	Cb_2O_5 .	ZrO_2 .	TiO_2 .	UO_2 .
IV.	1.46	36.39		25.00	10.06
V.	52.51		—	25.00	4.93*
VI.	3.20	28.70	4.23	23.70	7.50
VII.	—	—	63.36	29.92	—
	Ce_2O_3 .	Y_2O_3 .	PbO .	H_2O .	Total.
IV.	0.46	23.08	0.14	2.41	99.00
V.	7.40		—	11.14	100.98
VI.	—	23.12	0.14	6.41	100.12†
VII.	—	—	—	6.48	99.76

* UO_3 .

† Including iron oxide 3.12, SnO_2 trace.

L. J. S.

Analytical Chemistry.

Approximation in the Calculation of Chemical Analyses.
G. PANEBIANCO (*Gazzetta*, 1918, **48**, ii, 189—206).—Independently of experimental errors, the accuracy of analytical results is limited to two or three figures by the fact that the atomic weights of the

elements are exact to at most four, and more usually only three, figures. Various examples are considered, the values taken for the atomic weights and their absolute errors being those of the international table for 1911. Since $Sb=120.2$ and $S=32.07$, the percentages of these two elements in antimonite are 71.417 and 28.582 respectively. If, however, the values 120.2 ± 0.3 and 32.07 ± 0.01 are employed in the calculation, the limiting percentages for the antimony are 71.730 and 71.106, the absolute error being 0.5 (71.730—71.106); similarly, for the sulphur, the absolute error is 0.06%. Hence the percentage of antimony is accurate to only two figures, namely, 71, and that of sulphur to three figures, namely, 28.5.

The relative error, E , of an atomic or molecular weight may be expressed in the form of a fraction with 1 as numerator and some multiple of a power of 10 as denominator, that is, $1/h \cdot 10^n$. If, then, the value of this fraction is known relatively to an approximate number, of which the first significant number to the left is p , this number will have n figures exact if h is equal to or less than p , or $(n+1)$ figures exact if h is greater than p . Thus, for antimony with the atomic weight 120.2 and an absolute error e equal to 0.3, $E < 1/4 \cdot 10^2$; for antimony trisulphide, $E < (2 \times 0.3 + 3 \times 0.1)/(2Sb + 3S) = 0.63/333.61 < 1/5 \cdot 10^2$. Further,

for $100 \cdot 2Sb/(2Sb + 3S)$, $E_1 < E_1 + E =$

$$1/4 \cdot 10^2 + 1/5 \cdot 10^2 = 9/20 \cdot 1/10^2 < 1/2 \cdot 10^2,$$

and since $100 \cdot 2Sb/(2Sb + 3S) = 71.417$ and 2 is less than 7, only two digits, namely, 71, are accurate; similarly, for the percentage of sulphur, three digits are accurate.

A table is given showing for the atomic weights of the elements the absolute and relative errors. None of the latter is greater than $1/10^2$, and since for a compound the relative error must be less than the greatest of the relative errors of its constituent elements, such relative error of the molecular weight may be less than $1/10^2$.

The number of accurate digits in the percentages of the constituent elements of a compound may be rapidly established without calculation by application of the rule stating that the number of accurate digits of a quotient or product is one less than that of the term with the least number of accurate digits. Since no atomic weight has more than four digits exact, the percentage of any element or group of elements in a compound cannot have more than three digits accurate; further, such percentage cannot have less than two digits accurate (see above).

These considerations are extended by taking into account the weight of substance taken for analysis and the sensitiveness of the balance, the calculation of the error being employed to determine the minimum quantity of substance necessary to give the maximum accuracy in the digits of the percentage composition. T. H. P.

The Estimation of Solutions of Hydrochloric Acid and of Ammonia by Weighing Ammonium Chloride, and the Volatilisation of this Salt at Different Temperatures.

VICTOR AUGER (*Bull. Soc. chim.*, 1918, [iv], **23**, 467—472).—A reply to Villiers (compare A., 1918, ii, 332). W. G.

Estimation of Phosphorus and Silicon in Cast Iron.

ALFREDO CAVAZZI (*Annali Chim. Appl.*, 1918, **10**, 137—149).—The method of estimating phosphorus in cast iron (A., 1917, ii, 540) has been simplified in many of its details. The mixture of ferric sulphate with silica and carbon, separated as described, is boiled for about thirty minutes with dilute nitric acid (1:5) in a beaker over which is placed a retort containing cold water to act as a reflux condenser. The solution of ferric sulphate is filtered, the residue washed with water, acidified with nitric acid, and the orthophosphoric acid in the filtrate precipitated by means of ammonium molybdate. The precipitate is washed, dissolved, reprecipitated, and dissolved in ammonia solution, as described in the original method, and the solution is boiled with 3 grams of sodium chloride in order to precipitate any remaining iron as ferric phosphate. The precipitate is washed with boiling sodium chloride solution and fused with alkali carbonates, the mass treated with boiling water and filtered, and the filtrate acidified with nitric acid, treated with ammonia in slight excess, and added to the main solution. The phosphoric acid is then precipitated with magnesia mixture. The silica is estimated in an aliquot portion of the residue of carbon and silica by ignition over a blowpipe flame in a platinum crucible. [See also *J. Soc. Chem. Ind.*, 1919, March.] C. A. M.

Estimation of Arsenic in Ferro-molybdenum and other Alloys.

O. BINDER (*Chem. Zeit.*, 1918, **42**, 619).—The estimation of arsenic in ferro-molybdenum and similar alloys may be accelerated by carrying out all the operations in a long-necked Kjeldahl flask. The alloy is dissolved in nitric acid, the solution heated with sulphuric acid until acid fumes no longer appear, and then diluted, and the arsenic distilled from the same flask in the form of arsenious chloride. C. A. M.

Accurate Estimation of Carbon Monoxide in Gas Mixtures.

J. IVOR GRAHAM (*J. Soc. Chem. Ind.*, 1919, **38**, 10—14).—The author's experiments show that methods of estimation of carbon monoxide based on the reaction $5\text{CO} + \text{I}_2\text{O}_5 = 5\text{CO}_2 + \text{I}_2$ are capable of yielding exceedingly accurate results if certain precautions are observed. Two modes of procedure are adopted for the routine estimation of this gas, according as (a) the carbon monoxide content exceeds 0.2% and an accuracy of 0.02% is sufficient, or (b) the carbon monoxide content is about, or less than, 0.2% and a greater degree of accuracy than 0.02% is required. For the

analysis of samples as under (a), the apparatus described by the author and Winmill (T., 1914, **105**, 1996) is modified, mainly by replacing the beaker of water used for heating purposes by a small steam-bath, all burette readings being taken with the U-tube at the constant temperature of the steam-bath. Descriptions and sketches are given of the apparatus and of a portable form capable of estimating very much smaller quantities of carbon monoxide accurately to within less than 0.01%. The latter apparatus is varied slightly according as it is to be used in safety pits or in "naked-light" pits or other places. T. H. P.

Rapid Organic Combustions of Substances containing Nitrogen. HARRY L. FISHER and A. H. WRIGHT (*J. Amer. Chem. Soc.*, 1918, **40**, 868—869).—Reimer (A., 1915, ii, 578) has used cerium dioxide as a catalyst in the combustion of organic substances; cupric oxide is also employed, and, by the addition of lead peroxide and minium, carbon and hydrogen can be estimated in substances containing nitrogen. To prevent formation of cupric nitrate, the layer of cupric oxide must be maintained at a dull red heat; the lead peroxide-minium mixture is placed in the combustion tube about 5 cm. beyond the cupric oxide, and is heated at 300—320°. Several successive combustions may then be made in the same tube without changing the cupric oxide. W. P. S.

Methods of Water Analysis. ATILIO A. BADO, VICTOR J. BERNAOLA, AURELIO F. MAZZA, and LEOPOLDO DASSO (*Obras Sanitarias de la Nación, Buenos Aires*, 1918, 98 pp.).—A monograph giving a detailed account of the chemical and microbiological analytical methods in use in the Laboratorio de Análisis de Aguas y Ensayos de Materiales de las Obras Sanitarias de la Nación of Buenos Aires for the examination of potable waters.

W. S. M.

Rapid Method of Reduction of Potassium Platinichloride. HORSCH (*Compt. rend.*, 1919, **168**, 167—169).—In the estimation of potassium, the precipitate of potassium platinichloride, after being well washed with 80% alcohol, is dissolved in boiling water and the solution transferred to a weighed platinum crucible. Two to three c.c. of alcohol are added, and the whole heated on a rapidly boiling water-bath for twenty-five minutes, after which a few more drops of alcohol are added and the heating continued for five minutes. In this way, the platinum is deposited gradually and uniformly on the interior surface of the crucible, and is quite adherent. The liquid is poured out, the deposit washed with water, and the crucible is dried, ignited, and weighed. During the ignition, the deposit turns from black to a shiny, metallic appearance, and remains adherent. For the process, it is essential to use a platinum crucible, as the reduction only takes place in the presence of platinum, and the concentration of the potassium platinichloride solution must not exceed 0.25—0.30%. W. G.

Gravimetric Analysis. IX.—XI. Estimation of Calcium in the Presence of Phosphoric, Arsenic, and Boric Acids.

L. W. WINKLER (*Zeitsch. angew. Chem.*, 1919, **32**, i, 24).—Calcium is precipitated quantitatively as oxalate in solutions containing phosphoric, arsenic, and boric acids provided the solution is hot and that acetic acid and ammonium chloride are present. The following procedure is recommended. About 50 c.c. of solution, containing not more than 0.1 gram of calcium, are made slightly alkaline by the addition of ammonia, drop by drop. The solution is diluted to 100 c.c., and 3 grams of ammonium chloride added and allowed to dissolve; the solution is then acidified with 10 c.c. of *N*-acetic acid, and the calcium is precipitated as oxalate as prescribed for the pure solution. The last traces of precipitate may be removed from the beaker by means of a little pure methyl or ethyl alcohol, which is then poured on to the edges of the filter so as to wash them. The result may be corrected by a blank using a pure calcium salt. If a considerable portion of arsenic or phosphoric acid is present, a double precipitation is desirable, the first precipitate being allowed to remain overnight, collected, washed with ammonium oxalate solution, ignited, the residue dissolved in hydrochloric acid, and the calcium oxalate re-precipitated as before.

A. B. S.

Rapid Estimation of Lead in Brass and Alloys. G. H. HODGSON (*Chem. News*, 1919, **118**, 37—38).—A gravimetric and a volumetric method for the rapid estimation of lead in brass and similar alloys are described. The gravimetric method consists in precipitation of the lead as chromate from an acetic acid solution, conversion into sulphate, and finally weighing as molybdate. Five grams of the alloy are dissolved in 25 c.c. of nitric acid (D 1.4), the solution diluted with 200 c.c. of water, and sufficient aqueous ammonia (20 c.c., D 0.880) added to precipitate all the copper. Sufficient 80% acetic acid is then added to produce a clear, slightly acid solution, and 10 c.c. of 3% potassium dichromate are added, the mixture shaken, and kept for one hour. The precipitated lead chromate is filtered on a paper pulp pad and washed to remove the copper; hot douches of 30% sulphuric acid are poured on to the pad until the precipitate is entirely white. The sulphate is then washed with water. The lead sulphate is now dissolved by pouring about 40 c.c. of hot ammonium acetate solution containing acetic acid through the filter. The solution is raised to the boiling point and treated with ammonium molybdate. The precipitate is allowed to settle, filtered through an ashless paper pad, washed with water containing a little ammonium acetate, ignited, and weighed as lead molybdate. The whole process may be completed in four hours. The volumetric process consists in precipitation of the lead as chromate, as described above; the chromate precipitate is washed with water and warm dilute acetic acid (5%) until free from copper and the excess of potassium chromate. The chromate is dissolved by pouring 1:4 hydrochloric acid on to the

precipitate, and the pad finally washed with water to wash all chromic acid through. The free chromic acid may be estimated by titration with *N*/10-ferrous ammonium sulphate solution or by adding 10 c.c. of 10% potassium iodide solution and titrating the liberated iodine with *N*/10-sodium thiosulphate solution. The whole process may be carried out in two hours. Both methods have been compared with the gravimetric sulphate method, and found to give results in excellent agreement with those obtained by the better known method. J. F. S.

Unification of Methods for the Analysis of Cast Iron and Steel. A. MARINOT (*Ann. Chim. anal.*, 1919, [ii], 1, 5—10).—The following methods are suggested as being trustworthy. Total carbon may be estimated by Wiborg's method (combustion with sulphuric acid and chromic acid), by the ordinary method of combustion, or by the method described by Mahler and Goutal (A., 1912, ii, 807). Manganese is estimated by Traver's method (A., 1917, ii, 511), and phosphorus by the molybdate method. Sulphur is liberated as hydrogen sulphide in an atmosphere of carbon dioxide, collected in zinc acetate solution, and estimated iodometrically. Arsenic is also estimated iodometrically after distillation. [See, further, *J. Soc. Chem. Ind.*, March.] W. P. S.

Direct Estimation of combined Ferric Oxide in Silicates Insoluble in Acids. O. HACKL (*Chem. Zeit.*, 1919, 43, 9).—Knecht's volumetric method of estimating ferric salts by titration with titanous chloride, using potassium thiocyanate as indicator, is not directly applicable to silicates which have been decomposed with hydrofluoric acid. The influence of a small amount of this acid in preventing the appearance of the colour reaction with thiocyanate may be obviated by dissolving boric acid in the solution. This also restores the colour of ferric thiocyanate which has been destroyed by hydrofluoric acid; or methylene-blue, the colour of which is not affected by traces of hydrofluoric acid, may be used as indicator in place of potassium thiocyanate. C. A. M.

Estimation of Molybdenum. KUNO WOLF (*Zeitsch. angew. Chem.*, 1918, 31, i, 140).—When molybdenum is separated as its sulphide, and the latter then converted by ignition into molybdenum trioxide and weighed, the temperature during the ignition should not exceed 425°. The conversion of the sulphide into trioxide is complete at 400°; no further change takes place between 400° and 450°, but above 450° the trioxide sublimes. The correct temperature (400—425°) is most readily attained by using an electric furnace. W. P. S.

Emanation Method of Estimating Thorium. G. H. CARTLEDGE (*J. Amer. Chem. Soc.*, 1919, 41, 42—50).—It is shown by circulating a current of air through a thorium solution and an ionisation chamber until the activity has become constant

that the thorium content of any substance, which can be dissolved completely, may be estimated with an error which is not greater than 1.5%. In making the determination, it is advisable to draw air through the solution for some minutes, before connecting to the ionisation chamber, for the purpose of removing any radium emanation which may be present. It is also essential that the dimensions of the apparatus used should be the same in all experiments and that the temperature should be as nearly as possible the same. The method has been tested with a specimen of monazite sand, and it is found by this method that 8.61% of thorium oxide is present, whereas the gravimetric analysis indicates 8.57%. Details are given of a method of preparing a solution of monazite for this analysis. Two notes on the gravimetric analysis of monazite are appended to the paper. Carney and Campbell (A., 1914, ii, 583) use ammonium perchlorate and sulphuric acid for the destruction of the filter paper and the conversion of thorium pyrophosphate into thorium sulphate. This process may be carried out in one-half the time by using sulphuric acid and fuming nitric acid (D 1.53) instead. It is shown that the practice of using a slightly turbid, unfiltered solution of monazite in the analysis leads to high thorium results, since the titanium oxide is weighed along with the thorium.

J. F. S.

Estimation of Gold, especially in Animal Tissues.

SIDNEY M. CADWELL and GLADYS LEAVELL (*J. Amer. Chem. Soc.*, 1919, **41**, 1—12).—With the object of finding a method capable of estimating the amount of gold present in tissues, the authors have investigated the methods available for the estimation of gold, and have devised a method which, with a maximum error of 0.05 mg., is capable of estimating amounts of gold of 3.0 mg. and less. This method was required in connexion with the gold salt treatment of tuberculosis, and consists in placing 10 grams of fresh tissue in a 300 c.c. Kjeldahl flask, adding 10 c.c. each of concentrated sulphuric and nitric acids, and digesting over a free flame until the cooled solution is colourless. Air is then blown into the flask, and the mixture again heated until the volume of solution is reduced to 2 c.c.; this procedure removes most of the sulphuric acid. One c.c. each of hydrochloric and nitric acids is then added and the mixture boiled for a few minutes, and then a further c.c. of hydrochloric acid added. The solution is cooled, diluted with 5 c.c. of water, and concentrated ammonium hydroxide added until the colour is discharged, and then an excess of 2 c.c. The mixture is boiled, and the white precipitate which forms at this point dissolved by adding 5 c.c. of concentrated hydrochloric acid and boiling for three minutes. The solution is filtered through asbestos on an alundum plate, and the filtrate treated with ammonium hydroxide until it smells distinctly of ammonia. The volume of the solution should be now about 40 c.c.; 1.1 c.c. of 85% phosphoric acid and 0.75 gram of disodium hydrogen phosphate are added, and the solution electrolysed. A rotating anode and a cathode of

platinum sheet are used. The difference of electrode potential should be 0.9—1.2 volts, and the most efficient temperature is 60°. The method has been slightly modified to allow of its use for larger quantities of gold. By the addition of 6 grams of ammonium chloride to prevent precipitation, 30 to 40 mg. of gold can be electrolysed at 60°, with a voltage of less than 0.6 volt for the first thirty to forty-five minutes and below 1.3 volts for the remainder of the time, complete deposition usually requiring one and a-half hours. Under the conditions stated, gold can be completely separated from equivalent amounts of copper and iron, but the time required for electrolysis is greater than when these substances are not present. It makes very little difference whether the electrolysed solution is neutral or much more acid than stated above. The average time required for carrying out a complete analysis of gold by this method is less than two hours. J. F. S.

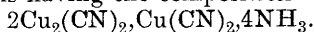
Quantitative Estimation of Sugar. A New Apparatus for the Estimation of Sugar in Urine. H. CITRON (*Münch. med. Woch.*, 1918, **65**, 1053; from *Chem. Zentr.*, 1918, ii, 869).—The author describes a simple apparatus for the estimation of sugar in urine according to Bang's method. H. W.

Quantitative Colorimetric Estimation of Pentosans in Meal. G. TESTONI (*Staz. sper. agr. Ital.*, 1917, **50**, 97—108; from *Chem. Zentr.*, 1918, ii, 865—866).—The method of Tollens and Krueger gives high results, because the starch is slowly but continuously converted into furfuraldehyde. Sucrose, maltose, and dextrose when heated with hydrochloric acid of the prescribed concentration also yield distillates from which phloroglucides are obtained. The hexoses, starch, and cellulose cause incorrect results in the estimation of methylpentosans, since, when treated with dilute mineral acid, they give, as intermediate product, ω -hydroxymethylfurfuraldehyde, which yields a phloroglucide, m. p. 95°, soluble in alcohol.

The author has therefore endeavoured to find a process by which the pentosans can be converted into pentoses easily identified by colour reactions, whilst the other constituents of the meal are not attacked in a vitiating manner. The most suitable reagent is a mixture of acetic acid (90 c.c.) and concentrated hydrochloric acid (D 1.19, 10 c.c.) at 45—50°. On addition of 0.25% phloroglucinol to this mixture, a red solution is obtained, which remains clear even when diluted with one hundred times its volume of water, and has well-marked absorption bands in the red, yellow, and blue. Different varieties of starch, dextrins, and different sugars have no influence on the reaction, whilst pentoses alone and in artificial mixtures are quantitatively found. The pentosans, even those contained in clover, are completely hydrolysed when heated for forty-five minutes with the reagent. H. W.

Action of Potassium Cyanide on Ammoniacal Copper Sulphate and its Application to the Estimation of Hydrocyanic Acid and Copper. L. JENNESSEAUX (*Ann. Chim. anal.*, 1919, [ii], **1**, 15—20).—Lassaigne's test for hydrocyanic acid (form-

ation of a white precipitate when a cyanide solution is treated with a drop of copper sulphate solution, then with sodium hydroxide solution, and the mixture acidified with sulphuric acid) may be rendered more sensitive if the copper sulphate solution is first treated with sodium hydrogen sulphite in quantity sufficient to change the colour from blue to green. When potassium cyanide solution is added to ammoniacal copper sulphate solution, a crystalline precipitate forms having the composition



Further addition of cyanide then causes the solution to become colourless, and the precipitate dissolves. This point is reached when a definite proportion of cyanide has been added, and the reaction may be used for the estimation of hydrocyanic acid, and, conversely, of copper. The copper sulphate solution used should contain 4.99 grams of the crystallised salt per 100 c.c., and this solution is mixed with 80 c.c. of *N*/1-ammonia and 20 c.c. of water; 10 c.c. of the mixture is a convenient quantity to take for an estimation. [See, further, *J. Soc. Chem. Ind.*, 1919, March.]

W. P. S.

Opium Analysis. D. B. DOTT (*Pharm. J.*, 1918, 101, 318).—The author deals with certain criticisms by Annett and Singh (*A.*, 1918, ii, 279) on the British Pharmacopœia method for the assay of opium by the lime-water process. Whatever may be the solvent influence of codeine on morphine in aqueous solution, the conditions of the assay process are entirely different, in that sufficient ether is added to hold in solution all the codeine possibly present. Moreover, the author has checked the alternative method proposed (*loc. cit.*), consisting in shaking the lime-water solution of the alkaloids with toluene to remove the codeine before precipitating the morphine by the official process. This alternative method (using benzene instead of toluene) gave a morphine precipitate heavier in weight and showing a higher titration value, but obviously less pure than the morphine prepared by the standard method. When the impurities were removed by washing with 80% alcohol saturated with morphine, the morphine prepared by the new process was no more than that prepared by the Pharmacopœia process, and there is no reason for altering the latter in the direction indicated by Annett and Singh.

J. F. B.

Separation and Estimation of Uric Acid and other Purines in Urine. F. TELLE (*Bull. Sci. Pharmacol.*, 1918, 25, 208—211; from *Chem. Zentr.*, 1918, ii, 770).—The uric acid is precipitated by the addition of solid ammonium chloride and ammonia to the acid urine, and, after collecting on a small filter, estimated by titration with permanganate in the presence of sulphuric acid. The purines in the filtrate are estimated by Denigès's method.

H. W. B.

Quick Estimation of Albumin (in Urine). A. SIMON and C. PAGEL (*Bull. Sci. Pharmacol.*, 1918, 25, 204—208; from *Chem. Zentr.*, 1918, ii, 767).—The urine is treated with saturated sodium

sulphate solution and two or three drops of acetic acid, and is then heated until the albumin separates in flocks. By means of the diaphanometer described in the original paper, the height of the liquid is determined at which a line drawn on the bottom of the vessel is no longer discernible. The amount of albumin in the urine can then be read off from the accompanying table. H. W. B.

Estimation of Urobilin in Urine. S. MARCUSSEN and SVEND HANSEN (*J. Biol. Chem.*, 1918, **36**, 381—389).—The presence of urobilin in urine may be readily detected by the following modification of Schlesinger's test. One gram of zinc acetate is weighed into a test-tube, and 10 c.c. of absolute alcohol are then added; 10 c.c. of the urine are placed in another test-tube, to which are added three drops of a 5% alcoholic solution of iodine. The contents of the two test-tubes are then mixed by repeated decantations until all the zinc acetate has dissolved. After filtering off the precipitate, the filtrate is found to be fluorescent if urobilin or urobilinogen was originally present in the urine.

By diluting the urine until fluorescence is no longer obtainable, a rough idea is furnished of the quantitative relationship of the urobilin. H. W. B.

The Estimation of the Nuclein Content of Yeast. C. A. LUBSEN (*Pharm. Weekblad*, 1918, **55**, (50), 1625—1628).—The hydrolysis of nucleoproteins by hydrochloric acid-pepsin solutions yields soluble albumins and an insoluble residue of nucleins; the latter contain 4—7% of phosphoric acid, representing the whole of the phosphorus present in the nucleoprotein. Further hydrolysis, for example, by trypsin, yields another albumin group, together with a nucleic acid. In analysing foodstuffs for nuclein content, Jebbink employs the pepsin-hydrochloric acid hydrolysis, using a solution containing 0.24% HCl, and determines the phosphorus in the insoluble residue of nuclein, using this as a measure of the nuclein content. Grijns criticises this method on the ground that so strong a solution of hydrochloric acid would cause further hydrolysis of the nuclein to the soluble nucleic acid, thus leading to low results.

The author has examined the question by carrying out experiments with yeast, using pepsin-hydrochloric acid solutions containing various proportions of hydrogen chloride. He finds that the weak solution (0.1% HCl) recommended by Grijns gives low results, owing to the slowness of the hydrolysis, whereas Jebbink's solution (0.24% HCl), and even stronger solutions (0.35% HCl), gives accurate results. It is therefore clear that the nucleins are not further hydrolysed by acid solutions of this strength, and Grijns's contention appears to have been wrongly based on the assumption that hydrolysis proceeded to the soluble nucleic acids. S. I. L.

General and Physical Chemistry.

Reversal of Spectrum Lines Produced by a Spark under Water. TOSHIKAZU MASHIMO (*Mem. Coll. Sci. Kyoto. Imp. Univ.*, 1918, **3**, 73—79).—The spectra of aluminium, zinc, cadmium, and mercury, produced by sparking between poles of these metals under water, have been examined down to $\lambda = 1850 \mu\mu$. It is shown that certain of the lines are reversed by this process; in the case of aluminium the lines $\lambda\lambda$ 1930, 1935, 2205, 2210, 2263, 2268, 2367, 2378, 2567, 2575, 2653, 2661, 3082, 3093, and $3944 \mu\mu$ are reversed. With zinc the lines $\lambda\lambda$ 2026, 2062, 2087, 2097, 2102, 2105, 2139, 2288, and 2832 (?) suffer reversal. Cadmium gives the lines $\lambda\lambda$ 2144, 2288, 3069, and $3095 \mu\mu$ reversed, whilst in the case of mercury the lines $\lambda\lambda$ 2482 and $2537 \mu\mu$ are reversed. J. F. S.

Effect of an Electric Field on the Spectrum Lines of Helium. II. TOSHIO TAKAMINE and NOBORU KOKUBU (*Mem. Coll. Sci. Kyoto. Imp. Univ.*, 1918, **3**, 81—92. Compare A., 1917, ii, 401).—Making use of Lo Surdo's method, the effect of electric fields (3000—70,000 volt per cm.) on the helium lines $\lambda\lambda$ 4169, 4144, 4026, 4009, 3965, 3868, 3830, 3820, 3614, 3448, and 2945 has been examined and the results compared with those of Stark, Brunetti, and Koch. It is shown that helium lines are effected in three ways by an electric field, (i) symmetrical resolution (λ 4686), (ii) non-symmetrical resolution (diffuse series of lines of helium and parhelium), (iii) one-sided displacement (principal series lines and sharp series lines of helium and parhelium). In the last-named case only the lines belonging to the principal series of parhelium are displaced toward the violet, whilst the other three series lines are displaced toward the red. Diffuse series lines are usually accompanied by an isolated component on the violet side, the starting point of which approaches more nearly to the initial line as the term number increases. The line λ 3830, the position of which was calculated by Koch, but not observed by him, appears in the photographs of some of the present experiments. Two lines, λ 2804 and 2482 Å.U., which are probably due to mercury, were also found to be displaced slightly towards the red in an electric field. J. F. S.

Investigation of Extreme Ultra-violet Spectra, with a Vacuum-grating Spectrograph. J. C. McLENNAN and R. J. LANG (*Proc. Roy. Soc.*, 1919, [A], **95**, 258—273).—A preliminary paper, in which a full description of a vacuum-grating spectrograph designed and made by the Adam Hilger Company is given. The theory of the concave grating is developed, and the experimental details for determining wave-lengths by means of this instrument are described. A short summary of the previous work in the extreme ultra-violet region precedes a description of the various

types of arcs used in the present examination of the extreme ultra-violet spectra of mercury, copper, iron, and carbon. The spectra were photographed on Schumann plates made by Hilger, and the wave-lengths are measured to within one Ångström unit. In the case of mercury nine lines appear in the photograph, lying between $\lambda=2054$ Å.U. and $\lambda=1435$ Å.U.; with copper thirteen lines appear between $\lambda=2243$ Å.U. and $\lambda=1925$ Å.U.; in the case of iron twenty-seven lines are found between $\lambda=2027$ Å.U. and $\lambda=1427$ Å.U.; carbon shows twenty-eight lines between $\lambda=2023$ Å.U. and 584 Å.U. Photographs of all the spectra are reproduced in the paper.

J. F. S.

Emission and Absorption in the Infra-red Spectra of Mercury, Zinc, and Cadmium. RAYMOND C. DEARLE (*Proc. Roy. Soc.*, 1919, [A], 95, 280—299).—The absorption spectra of mercury, zinc, and cadmium have been measured in the infra-red region; for the region up to 8500 Å. the spectrum was photographed, whilst above this wave-length a linear thermopile and galvanometer were used. The light was obtained from a mercury amalgam lamp of the Heraeus type; the amalgam consisted of 60% mercury, 20% lead, 20% bismuth, $\frac{1}{2}$ % zinc, and $\frac{1}{2}$ % cadmium. In some cases an arc of the metal in a vacuum was employed. For the energy measurements a 100 volt Nernst glower was used. In the case of mercury absorption bands $\lambda=1\cdot014\ \mu$, $1\cdot038\ \mu$, $1\cdot065\ \mu$, $1\cdot089\ \mu$, $1\cdot129\ \mu$, $1\cdot160\ \mu$, $1\cdot207\ \mu$, and $1\cdot359\ \mu$ were observed. Energy measurements were made in the region $1\cdot2$ — $1\cdot5\ \mu$, the only absorption band observed lying at $\lambda=1\cdot359\ \mu$. No absorption was shown in the case of the energy measurements of zinc until the temperature had been raised to 275° . At this temperature absorption was observed at $\lambda=1\cdot105$; in the longer wave-lengths evidence was more difficult to obtain, but indications of absorption were obtained at $\lambda=1\cdot379\ \mu$, $1\cdot41\ \mu$, $1\cdot57\ \mu$, and $1\cdot65\ \mu$. With cadmium vapour absorption was found at $\lambda=1\cdot040\ \mu$, which is the first line of the series $\nu=(2\cdot5S)-(m,P)$; a second strong absorption band occurs at $\lambda=1\cdot503\ \mu$, whilst less marked absorption occurs at $\lambda=1\cdot129\ \mu$, $1\cdot395\ \mu$, $1\cdot4475\ \mu$, $1\cdot522\ \mu$, and $1\cdot563\ \mu$. By the photographic method a line was observed at $6977\cdot4$ Å. in one series of experiments, but this line could not be reproduced. Some absorption experiments were carried out with a quartz cell containing cadmium iodide; it was found that there was no absorption in the visible and ultra-violet regions at comparatively low temperatures, but with increased temperature a broad band was observed which extended from the limit of the ultra-violet end of the spectrum up to a wave-length of about $\lambda=4000$ Å. Attempts to resolve this band failed. In the longer wave-lengths no absorption was visible at wave-lengths characteristic of the cadmium spectrum. Energy measurements made in the long wave-length region above $\lambda=1\cdot0\ \mu$ showed the presence of an absorption band at $\lambda=1\cdot040$ when the temperature of the cell was above that necessary for dissociation. The emission and absorption curves obtained by bombarding mercury vapour

with electrons with the object of producing the single line spectra are given. J. F. S.

Characteristic Ultra-red Vibrations of Diatomic Crystals.

M. BORN (*Physikal. Zeitsch.*, 1918, **19**, 539—548).—A mathematical paper, in which the relationship between the constants of a diatomic regular crystal grating is considered. The influence of electrons on the index of refraction in the ultra-red is also considered mathematically. The results obtained are applied to crystals of rock salt, sylvine, potassium bromide, potassium iodide, pyrites, fluorspar, and sodium chlorate. J. F. S.

Absorption Spectra and the Ionisation Potentials of Calcium, Strontium, and Barium. J. C. McLENNAN and J. F. T. YOUNG (*Proc. Roy. Soc.*, 1919, [A], **95**, 273—279).—The absorption spectra of calcium, strontium, and barium have been determined, and from the values of the wave-lengths the ionisation potential of these elements calculated. In the case of calcium a hollow carbon filled with metallic calcium was used, and it was observed that the reversals were confined entirely to those wave-lengths which were members of the series $\nu = (1.5S) - (m, P)$; as given by Lorenser (*Inaug. Diss.*) these are:

$m =$	2.	3.	4.	5.	6.	7.
$\lambda =$	4226.91	2721.77	3298.66	2275.60	2200.8	2151.00
$m =$	8.	9.	10.	11.		
$\lambda =$	2118.99	2097.8	2083.2	2072.8		

In the case of strontium the sulphide was employed instead of the metal, and the wave-lengths for $\nu = (1.5S) - (m, P)$ also accord with those of Lorenser. The following were found:

$m =$	2.	3.	4.	5.	6.
$\lambda =$	4607.52	2931.98	2569.60	2428.16	2354.40
$m =$	7.	8.	9.	10.	11.
$\lambda =$	2307.5	2275.5	2253.5	2237.4	2226.0

In the case of barium the oxide was used, and by noting the reversals nine members of the series $\nu = (1.5S) - (m, P)$ were obtained; these are:

$m =$	2.	3.	4.	5.	6.
$\lambda =$	5535	3275	2845	2597	2542
$\nu =$	10864.6	30534.4	35149.4	38502.1	39339.1
$m =$	7.	8.	9.	10.	
$\lambda =$	2498	2470	2455	2441	
$\nu =$	40032	40486	40733.2	40966.8	

From the limiting frequencies of the single series of the spectra the following ionisation potentials of the vapours have been calculated: mercury, 10.45 volts; zinc, 9.4 volts; cadmium, 9.0 volts; magnesium, 7.65 volts; calcium, 6.12 volts; strontium, 5.7 volts; and barium, 5.21 volts. J. F. S.

Changes in Spectrum Intensity and Weakening of the Iodine Fluorescence by means of a Magnetic Field. W. STEUBING (*Ann. Physik*, 1919, [iv], 58, 55—104).—In a previous note (*Verh. deut. physikal. Ges.*, 1913, 1181) it was shown that when fluorescent iodine vapour is brought between the poles of a powerful electric magnet, the intensity of the fluorescent light is greatly diminished. The present paper deals with the investigation of this phenomenon. The light changes have been investigated spectrophotometrically and spectrographically, and a series of energy measurements have also been made. It is shown that it has been impossible to attribute the weakening of the iodine fluorescence to any definite cause, but that it depends on the action of a magnetic field on the electron vibrations which give rise to the emission of a band spectrum. The effect is greater with the higher frequencies than with the lower, and, further, the magnetic field has a more pronounced action the greater the vibration amplitude during the emission. The present phenomenon, therefore, has nothing in common with other processes which diminish or destroy fluorescence. The magnetic action has little to do with the actual fluorescence, and the same effect is to be expected if the same band spectrum is produced in some other way; it is to be expected that the magnetic weakening will take place more easily the greater the energy per molecule with which the emission occurs, and consequently an electrically produced spectrum will be correspondingly more strongly weakened by weaker magnetic fields. J. F. S.

The Magnetic Field and the High Frequency Spectrum of the Elements. RITA BRUNETTI (*Nuovo Cim.*, 1918, [vi], 16, ii, 5—18).—Assuming that the action of a magnetic field results in decomposition of high frequency radiations, the results of the author's experiments show that the ordinary means of spectral analysis would be insufficient to reveal directly such decomposition, if the latter were of the type and order of magnitude of the Zeeman phenomenon. None of the theories on the emission of high frequency radiations excludes the possibility of a decomposition produced in this manner. The lines of the *K* spectrum for iron, nickel, and copper are found by the curved crystal method to be double, the mean difference between the two components being 8/1000 and 11/1000 Ångström units for the α and β lines respectively. No qualitative modification of any kind is exhibited in the characteristic spectra of these elements under the influence of magnetic fields of moderate magnitude and degree of variation. T. H. P.

Light Positive and Light Negative Photophoresis [in Connexion with] Sulphur and Selenium. IRENE PARANKIEWICZ (*Ann. Physik*, 1918, [iv], 57, 489—518).—It has been shown by Ehrenhaft (*ibid.*, 1918, 56, 81) that particles of matter fall under the action of gravity, but rise in an electric field; some particles when subjected to a strong beam of light are deflected, in the horizontal direction, from their original path. Thus sulphur particles

move in the direction opposite to that of the beam of light (light negative); selenium particles under some conditions move in the direction of the beam of light (light positive). The present paper is a continuation of this work, and deals with the dependence of the photophoresis on the chemical nature of the particles, the intensity of the light, pressure of the surrounding medium, and the size of the particles. The work has been carried out with sulphur and selenium particles of radius $8-60 \times 10^{-6}$ cm. The methods adopted in the investigation were similar to those employed by Ehrenhaft. It is shown that sulphur particles are always light negative, whereas selenium particles are either light negative or light positive, depending on the duration of heating in the production of the particles. The light negative photophoric force on selenium particles is approximately six times as great as the force of the same light beam on sulphur particles of the same mobility. The intensity, with which particles of a given material react on the light, is dependent on the size of the particles. The negative photophoresis shows its maximum action on sulphur particles of radius 27×10^{-6} cm., and on selenium particles of radius 15×10^{-6} cm. The photophoric force on sulphur and negative selenium is independent of the time, whilst with positive selenium it is a function of the time. The power of reaction on the light of positive selenium decreases with time. The photophoric force is independent of the surrounding gas and also of the pressure. The independence of the photophoric force on the pressure, the chemical nature of the surrounding gas, the decrease of the positive reaction of selenium particles which is due to an internal change of the selenium, and, further, the fact that particles of different materials, but of the same mobility, are very differently acted on by light, all tend to confirm the conclusion of Ehrenhaft that the action is a direct one of the light on the material.

J. F. S.

X-Ray Spectra and the Constitution of the Atom. II.

L. VEGARD (*Phil. Mag.*, 1919, [vi], **37**, 237—280. Compare A., 1918, ii, 144).—A theoretical paper, in which the process of recombination of the primaries is discussed, together with some of the consequences which follow from them. Calculations are made of the quant-number and the number of electrons of the ring systems from the observed frequencies. The possibility of there being two *L* and two *M* rings is considered. It is shown that whether recombination is assumed from a normal or deformed primary system, or recombination from a secondary one, it must be assumed that the angular momentum of the electrons left behind in the atom remains unchanged; and further it must be assumed that the changes of energy of the systems situated between the broken ring and the ring of departure enter into the energy quantum of radiation which is emitted as the result of recombination. On the basis of the theory of the production of X-rays developed by the author it must follow that recombination takes place from secondary systems, and that always the angular momentum of the electrons left behind

in the atom is kept constant during expulsion and recombination. A number of relationships of the atomic constitution and properties of the atoms are given. All elements belonging to the same period of the periodic classification have the same quant-number, and this number increases by one unit on passing from one period to the next.

J. F. S.

Radioactivity and the Coloration of Minerals. EDGAR NEWBERY and HARTLEY LUPTON (*Mem. Manchester Phil. Soc.*, 1918, **62**, No. 10, 1—15).—The colours obtained on exposing various substances to the action of the β - and γ -rays of radium, and sometimes to the α -, β -, and γ -rays of the radium emanation, are recorded. Various differently coloured fluorspars, owing to their wonderful range of colours and remarkable thermo-luminescence, proved the most interesting, the changes produced by radium being so varied as to be bewildering. A colourless Matlock fluorspar after twenty-four hours' exposure to 50 mg. of radium became blue, deeper than a copper sulphate crystal, the colour being permanent in the dark but destroyed by direct sunlight, or, more slowly, by daylight and by gentle heating, but the fluorspar may be recoloured by radium indefinitely. Under cathode rays, only a faint purple surface colour was produced. The blue colour is probably due to the γ -rays, as it penetrates right through the crystal. The thermo-luminescence was green and feeble, but a Pyrenean fluorspar, not coloured by radium, gave a remarkable and lasting green light on heating, even though only exposed 150 mm. away from the radium. The thermo-luminescence of Cornish chlorophane is to be ascribed to γ -rays from radioactive materials. On crystal quartz there was no sign of the "rotting" produced by radium rays in fused quartz. The natural colours are discharged by heating, but may be restored by radium.

Clear selenite crystals were coloured brown in regular figures, the remaining parts being colourless, a phenomenon which Miers explains by certain faces of the crystal during growth attracting impurities, to which the colour is to be ascribed. Among other substances examined were diamond, native sulphur, cryolite, rock-salt, sylvine, ruby, anhydrite, celestine, barytes, anglesite, apatite, phosphorite, topaz, zircon, beryl, kunzite, calcite, glass, and bakelite, an artificial amber-like material used for electric insulation. The view that the colours are due to dissociation of minute traces of impurities and the luminescence to the recombination of the products of dissociation is favoured.

F. S.

Dependence on Temperature of the Dielectric Constant of some Gases and Vapours. MARIO JONA (*Physikal Zeitsch.*, 1919, **20**, 14—21).—The dielectric constant of air, carbon dioxide, ammonia, sulphur dioxide, methyl alcohol vapour, and steam has been measured at a series of temperatures from 17.8° to 178.1°. Curves of the variation of the constant with temperature are given, and the significance of the curves is discussed mathematically.

J. F. S.

Significance of the Volta Effect in Measurements of Electromotive Equilibria. A. SMITS and J. M. BIJVOET (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 562—569).—Application of the more recent views of electromotive equilibria to the Volta effect leads to the result that, on polarisation and passivation, the change in this effect must be great, and that in these phenomena the Volta effect would constitute even the greatest part of the total change in the electromotive force. It is found, further, that if the Volta effect between metals in which the state of internal equilibrium prevails are really very small, as is rendered probable by recent experimental work, this must be regarded as a characteristic property for metals in internal equilibrium.

The values found on measurement of potential differences for metal-electrolyte, termed experimental electrical potentials, always contain an unknown Volta effect, and it is this which renders impossible calculation from the said potentials of the saturation concentrations of the metal ions.

Relations have been derived which contain the solubility product of the metal, the solubility quotient of the non-metal, or the electron concentration in the electrolyte, but not the Volta effect, and these permit of the preparation of a solubility product series of metals and a solubility quotient series of non-metals, from which conclusions may be drawn as to the chemical and electrochemical behaviour of the metals.

T. H. P.

Hydrogen Overvoltage. DUNCAN A. MACINNIS and LEON ADLER (*J. Amer. Chem. Soc.*, 1919, **41**, 194—207).—None of the theories advanced to account for overvoltage, with the exception of that of Möller (A., 1909, ii, 114), attempts to explain the great influence exerted by the physical condition of the electrode on the overvoltage, a polished platinum electrode, for instance, showing an overvoltage as high as 0.1 volt, whereas that for platinised platinum is nearly zero. The authors have made a number of measurements of hydrogen overvoltage with platinised platinum electrodes, use being made of an apparatus resembling, but differing in detail from, that of Thiel and Breuning (*Zeitsch. anorg. Chem.*, 1913, **83**, 329). With such low currents that one bubble of hydrogen appears in one or more minutes, fluctuations in the overvoltage are observed, the curve connecting overvoltage with time being sinuous with a sharp break invariably following the highest voltage. At low current densities, the bubbles come off at one point and continue to do so, no matter how long the observations are continued, so that each bubble probably leaves a nucleus behind it when it becomes detached.

In explanation of these results, it is assumed that molecular hydrogen, when formed from hydrogen ions by the reaction $2\text{H}^+ + 2\epsilon = \text{H}_2$, goes directly into solution in the electrolyte immediately surrounding the electrode, so that the hydrogen at that point will tend to rise in concentration and produce a supersaturated solution unless carried away by diffusion, stirring, or other means. If.

however, a nucleus of gaseous hydrogen is present in the electrode, a portion of the hydrogen will enter this gaseous phase, either directly from the electrode or by absorption from the electrolyte, the gaseous nucleus thus playing a part similar to that of a small crystal in a supersaturated salt solution. Hydrogen gas in the form of small bubbles must have a higher energy content per mol. of gas than the same volume of undispersed gas, as energy must be expended in overcoming the surface tension in the formation of small bubbles. Such bubbles will be more soluble, that is, will remain in equilibrium with more concentrated dissolved hydrogen, than the undispersed gas, this phenomenon being analogous to the increase in solubility produced by the fine grinding of solids. Since, other factors being constant, the potential at a hydrogen electrode depends primarily on the concentration of the dissolved hydrogen, an electrode in equilibrium with the small bubbles will reach a higher potential than a similar electrode in equilibrium with the undispersed gas. As electrolysis proceeds and the nucleus of gaseous hydrogen grows, the energy necessary to produce further growth must decrease, since the value of the ratio, increase in surface:increase in volume, is continually decreasing; if the bubble grows slowly, the hydrogen-bearing solution surrounding the electrode will tend to get into equilibrium with the bubble. This accounts for the decrease in overvoltage from a maximum point of the sinuous curve to a minimum point, where the buoyant effect of the solution is sufficient to overcome the attraction of the electrode for the bubble, which breaks away, leaving a nucleus behind. On the rising part of the curve, the concentration of the dissolved hydrogen is increasing to a value such that the nucleus can again grow, and so on. As the bubbles are not always evolved at the minimum points of the curve, it seems probable that, since the nuclei tend to form in depressions in the electrode, the bubbles that separate from the nuclei remain in these depressions until forced out by the growth of succeeding bubbles.

If the electrode can adsorb large hydrogen gas nuclei to start bubble formation, the supersaturation cannot rise to high values and the electrode will have a low overvoltage, metals with small adsorptive powers, however, hold small nuclei and have high overvoltages.

Support of the above explanation is furnished by microscopic examination of various electrodes when evolving hydrogen, this indicating experimental agreement with a theoretical quantitative relation between the size of the bubbles from, and the overvoltage of, platinised platinum electrodes. Further, theory indicates that the overvoltage should increase as the pressure decreases, and this is shown to be the case by the authors' results and also by unpublished work of H. M. Goodwin and L. A. Wilson. T. H. P.

The Modality of Reactions and Chemical Dynamics; Application to the Phenomena of Electrolysis and Spectroscopy. J. MEUNIER (*Bull. Soc. chim.*, 1919, [iv], 25, 49—68).—The

chemical dynamics are the same, in principle, in the different forms of electric cells, which only differ amongst themselves in their complex and variable, secondary reactions. There is the same analogy in the production of spectral rays. The appearance of rays in the spectrum does not characterise, as is usually stated, an element, but rather a reaction of this element, and consequently indicates the presence of another element reacting with it. W. G.

Theory of Specific Heat. II. WALTER JANKOWSKY (*Zeitsch. Elektrochem.*, 1919, **25**, 1—3. Compare A., 1918, ii, 59).—The author answers the criticism of Drucker (A., 1918, ii, 216) made in connexion with the earlier paper, and a further development of the theory of specific heat is contributed. It is shown that the statement that the change of the specific heat with temperature disproves the law of Dulong, Petit, and Joule is incorrect, for in every case regular relationships exist between the specific heat, the number of atoms, and the molecular weight. J. F. S.

Specific Heat Determinations at Higher Temperatures. WALTER P. WHITE (*Amer. J. Sci.*, 1919, [iv], **47**, 44—59).—In determining the specific heats of various substances at temperatures up to 1400° by the method of mixtures, the errors in the final result frequently approach one part per thousand even with precise work. The chief sources of error are: (1) the determination of temperature in the furnace, (2) the loss of heat during the dropping of the charge, (3) the exposure of the calorimeter to the atmosphere during the drop, (4) the effect of external conditions on the calorimeter, and (5) internal effects, such as auxiliary changes in the interior of the calorimeter after the drop.

Of these errors, the variability of the heat losses attending the dropping of the hot substance into the water is surprisingly great and should be prevented.

Modifications in furnaces and in methods of transference to the calorimeter are described in detail. [See, further, *J. Soc. Chem. Ind.*, 1919, 158A.] A. B. S.

Specific Heats of Silicates. II. WALTER P. WHITE (*Amer. J. Sci.*, 1919, [iv], **47**, 1—43. Compare A., 1909, ii, 966).—The specific heats of various silicates at various temperature intervals from 0—1400° were determined, using the method of mixtures, with greater precision than hitherto.

For quartz and silica glass, the values of the interval specific heats satisfy the expressions:

Quartz	$0.1685 + 0.000194\theta - 0.00000011\theta^2$
Silica glass.....	$0.1670 + 0.000189\theta - 0.000000125\theta^2$

The "instantaneous," or true atomic heats, rise regularly from about 3.5 at 0° to about 5.96 (with anorthite to 6.6) at 1300°, the value given by the classical kinetic theory.

The variations of the atomic heat from the theoretical constant

are due partly to secondary thermal effects connected with expansion, change of state or chemical action, and partly to the universal tendency towards a maximum value at a high temperature. The location of the development curve agrees approximately with the values of the atomic vibration frequency, calculated from the known properties of the atoms.

The difference in the value of the elements and compounds shows that it is not a property of the atom, but appears to be related to the combined oxygen.

The calculated specific heat of silica glass at constant volume and that at constant pressure are equal, but the actual heat-temperature curve of silica glass above 600° is above the theoretical value; that of the cristobalite is identical with the theoretical curve at 900° , but then rises above it. With albite and microcline, the specific heat at constant pressure is considerably above the specific heat at constant volume, and this confirms the evidence that the theoretical value of the dimension constant A in the expression $C_p - C_v = [A(3a)^2 \Theta] / Kd$ is exceeded at high temperatures.

On comparing the specific heats of various silicates in the crystalline and glassy form, respectively, it was found that the specific heat of the glass is seldom greater than that of the crystal.

A. Smits' attempts to correlate inversion with equilibrium-temperature changes in liquids or liquid and solid systems have been examined with negative results, and it is suggested that premature fusion due to impurities and sluggishness of transformation account for the observed phenomena.

The conclusion is drawn, from the expansion and specific heats of solids being much less anomalous and irregular than those of liquids, that the molecular changes in solids are of a different order of magnitude. The author partly agrees with Bridgman that there is no relation between the volume, specific heat, and cohesion of pre-inverted and inverted substances, but considers that the change of properties during inversion, although rapidly accelerated at times, is nowhere sudden and discontinuous.

The observed difference in the atomic heat of different crystalline forms of the same substance is so irregular that similar differences with substances of unlike composition must be interpreted cautiously. [See, further, *J. Soc. Chem. Ind.*, 1919, 140A.]

A. B. S.

Specific Heat of Aqueous Solutions with Special Reference to Sodium and Potassium Chlorides. W. R. BOUSFIELD and C. ELSPETH BOUSFIELD (*Phil. Trans.*, 1919, [A], 218, 119—156).—The specific heat of aqueous solutions of sodium chloride and potassium chloride of various concentrations has been determined by the same method and using the apparatus previously described (A., 1911, ii, 580). In each case, the mean specific heat over the temperature ranges 0 — 13° , 13 — 26° , and 26 — 39° was determined. The results of the present work indicate that the specific heat and

specific volume of the combined water may be treated as approximately constant, and the lowering of the specific heat and specific volume of the free water on the introduction of a solute are each proportional to the percentage concentration of the solute. In dilute solutions, the specific heat curve approximates to that of water, which has a minimum at about 25° . In concentrated solutions, the variation of the specific heat with temperature appears to follow an almost straight line law. This behaviour is attributed to the simplification of the water by a considerable destruction of ice and steam molecules, and is analogous to the corresponding phenomenon noted previously (Bousfield and Lowry, A., 1905, ii, 135). The relationship $(dQ/d\theta)_H = L(d\chi/dH)_Q$ is found between the heat of dilution and the contraction. The following constants have been derived: (i) for potassium chloride: the specific heat of the liquid solute, 1.655; the molecular heat of the liquid solute, 123.4; (ii) for sodium chloride: specific heat of the liquid solute, 2.433, and the molecular heat of the liquid solute, 142.1. The number of molecules of water combined with a molecule of solute is calculated for various dilutions. J. F. S.

Neumann-Kopp's Law. FRIEDRICH BÜRKI (*Helv. Chim. Acta*, 1919, 2, 27—38).—For a number of the elements, the difference, $C_p - C_v$, between the atomic heats at constant pressure and at constant volume has been calculated by means of the formula $C_p - C_v = Ta^2V/41.89x$ cal., where V is the atomic volume, a the coefficient of cubical expansion, and x the coefficient of compressibility; for chemically related elements, the differences are, as a first approximation, the same.

In the case of the haloids of the elements of the first group of the periodic table, the Neumann-Kopp law is more exactly fulfilled for molecular heats at constant pressure than for molecular heats at constant volume. C. S.

Determination of Melting Points by means of Electric Heating. SIEGFRIED LAURENS MALOWAN (*Zeitsch. angew. Chem.*, 1919, 32, i, 16).—Two test-tubes are fastened concentrically one inside the other, leaving a small air-space at the sides and 15 mm. between the bottoms of the tubes. The inner tube is provided with a two-holed rubber stopper, one hole for the thermometer, the other for slipping in the melting-point tube. For making a melting-point determination, the apparatus is fixed with the bottom of the outer tube 5 mm. inside the mouth of a small electrically heated Heraeus crucible furnace. It is claimed that the temperature control is better and the results more accurate than with the usual forms of melting-point apparatus, and, in addition, the whole apparatus can be very quickly cooled. E. H. R.

Boundaries of Existence of the Liquid State. G. BRUNI (*Atti R. Accad. Lincei*, 1918, [v], 27, ii, 394—397).—The author criticises the conclusions drawn by Herz (A., 1918, ii, 150), who, like Meyer (A., 1918, ii, 292), has overlooked the fact that the true

melting point (triple point, solid-liquid-vapour) does not delimit the liquid state at its lower boundary, the melting point varying with the pressure. Herz considered only twenty-two out of eighty-eight elements, and his deductions have neither theoretical bearing nor empirical confirmation. T. H. P.

Application to Eight Different Substances of the Formula which Expresses the Heat of Vaporisation of a Liquid.

E. ARIÈS (*Compt. rend.*, 1919, **168**, 444—447).—Using the formula previously given (compare *ibid.*, 204), the author has calculated the heat of vaporisation for carbon dioxide, ammonia, stannic chloride, methyl formate, pentane, hexane, heptane, and octane, and finds that the calculated results agree very well with those obtained by different workers. W. G.

Limits of Separation by Fractional Distillation: A New Still-head. S. F. DUPTON (*J. Soc. Chem. Ind.*, 1919, **38**, 45—46*t*).

—The still-head described consists of an open tube inside which is another, closed, one with a wire wound spirally round it so that it just fits the outer tube. The latter may be made of parts of different sections increasing in diameter downwards, this gradation of the annulus serving to carry away the increasing volume of condensed liquid; a form more easily constructed consists of one length of tubing of approximately uniform bore, the spirals being wound on cores of decreasing diameter. For any particular set of conditions, there is a certain minimal value for the working volume of the still-head; if this is exceeded, there is no consequent increase in the amount of inseparable mixture in the still-head, the extra length at the bottom becoming filled with vapour and liquid of one of the pure constituents. Such still-heads are far more efficient than the Young pear-bulb column in common use, and have the great practical advantage that the distillation, having been started at the proper rate, slows down and stops when the limit of each pure constituent is reached, rise in the temperature being then necessary to drive off the next constituent. From a mixture of 5 c.c. of benzene with 10 c.c. of toluene, 4.6 c.c. of benzene and 9.4 c.c. of toluene were recovered by direct distillation; the loss was 0.3 c.c. and the unseparated intermediate portion 0.7 c.c., which is not far removed from the actual working volume, the total volume found in the flask at the end of the operation being just twice this amount.

A similar arrangement provides a very efficient means of washing a gas with a small quantity of liquid. In this case, the annulus is made of the same size throughout, and the pitch of the wire spiral is kept as small as practicable so as to reduce the speed of descent of the liquid. Such a washer gives more intimate average contact between gas and liquid and introduces no hydrostatic pressure. T. H. P.

Ultramicroscopic Examination of very thin Deposits, of Metals and Salts, obtained by Evaporation in High Vacua.

L. HAMBURGER (*Kolloid Zeitsch.*, 1918, **23**, 177—199).—The thin

deposits produced on the walls of a vessel in which metals and other substances have been strongly heated have been examined by means of an ultramicroscope. The metals were mounted in the form of thin wires and heated electrically in a vacuum; salts, such as sodium chloride and calcium fluoride, were heated on a tungsten wire. It was found that on admitting air to the cooled vessel, changes in the nature of the film occurred, and in consequence the film was protected by a thin layer of Canada balsam before air was admitted and the ultramicroscopic examination made. The experiments were carried out with the metals silver, gold, tungsten, molybdenum, platinum, iron, copper, nickel, magnesium, zinc, and cadmium, and also with carbon, sodium chloride, and calcium fluoride. It is shown that the metals with high melting points, molybdenum, platinum, nickel, and iron, and also carbon, produce sublimates which are either completely unresolvable or mainly unresolvable into particles. The lower melting elements with a higher vapour tension, gold, silver, copper, magnesium, zinc, and cadmium, show a greater tendency to a less disperse condensation and produce a complete network of ultramicros. Generally, it can be stated that the higher the temperature necessary for slow sublimation the finer is the structure of the sublimate. The electrical conductivity of films of gold, silver, platinum, and tungsten of measured thickness has also been determined, and it is shown that a covering of calcium fluoride or Canada balsam is a very efficient protection for these metals. Films condensed at the temperature of liquid air, on warming to the ordinary temperature, undergo a non-reversible change of resistance, which is very great in the case of gold and silver. This is probably due to a change in the structure of the deposit, for ultramicroscopically the deposits are seen to be different at the two temperatures. Many deposits undergo a change of resistance when there is no temperature change. In particular, silver deposits produced and kept at the ordinary temperature for long periods increase in their resistance to an infinitely large value. This must be due to changes in the optically unresolvable part of the deposit which lies between the network. These changes are probably of such a nature that small gaps occur, and consequently the direct metallic contact is broken. The influence of the temperature of the walls on which the deposit is formed has been investigated, and it is shown that the higher the vapour tension of the metal is at the temperature of the walls, the less disperse is the structure of the deposit. Many of the metals produce films of definite colours which are characteristic of the metal and are determined by the selective absorption of light by the atoms.

J. F. S.

Evaporation and Condensation Velocities and the Calculation of Chemical Constants from the Density of the Condensate. MAX TRAUTZ (*Zeitsch. anorg. Chem.*, 1919, 105, 97—111).—A mathematical discussion of the equilibrium between vapour and liquid treated as a simple chemical reaction. From the

gas theory and the thermodynamic laws, formulæ are developed expressing evaporation and condensation velocities in terms of heat of evaporation, molecular heat, molecular weight, molecular diameter, density of the condensate, and closeness of packing. The chemical constant of the "reaction" is the logarithm of the ratio of the maximum evaporation and condensation velocities. It increases with increasing molecular diameter, with decreasing molecular volume, and with decreasing density of packing of the molecules. With increasing molecular weight the constant first rises and subsequently falls continuously. It is shown that all the factors involved in the calculation of the evaporation and condensation velocities can be given a purely mechanical interpretation, with the exception of the heat of evaporation. For the first time a purely mechanical interpretation of the chemical constant is given, its calculation requiring only the molecular diameter, molecular weight, and density.

The method of investigation here used, involving a mathematical analysis of the processes occurring at the surface between two phases, is applicable to other problems, such as the solution of gases in liquids and diffusion problems.

E. H. R.

The Extension of the Gas Laws to Liquids and Solids.

JOHN SCOTT HALDANE (*Biochem. J.*, 1918, **12**, 464—498).—The three gas laws may be combined and more correctly stated, and at the same time extended to liquids, in the form: The intermolecular volume of a given volume of gas or liquid varies inversely as its mean intermolecular pressure, and directly as the absolute temperature, the concentration of gram-molecules, and a constant which is the same for all gases and liquids. This may be embodied in the equation $P(V-v)=22.4nT/273$ or $P(V-v)=0.082nT$, where P =mean intermolecular pressure in atmospheres, V =volume in litres, v =volume virtually occupied by the molecules themselves, n =relative number of molecules, so that when P and $n=1$ and $T=273^\circ$ absol., $P(V-v)=22.4$. This casts new light on the physical properties of solutions and on various phenomena connected with gases and liquids. Thus it can be shown that: (a) Diffusion pressure of any one substance between one liquid or gas and another is proportional to the values of its partial pressures p in the one liquid or gas, and $1-v$ in the other. (b) The intermolecular pressure is the same for all solutions in the same solvent, up to high concentrations and with wide variations of temperature. (c) Osmotic pressure is simply the increased intermolecular pressure required to neutralise the excess of diffusion pressure of a pure solvent inwards over that of a diluted solvent outwards, through a membrane permeable to the solvent, but not to the solute which dilutes it. This excess is given by the equation

$$p_0=0.082NT(n/N_1-n),$$

where p_0 =osmotic pressure and n, N, N_1 =gram-mols. of solute, pure solvent, and solution per litre. (d) Diminution of vapour pressure of the solvent and rise of vapour pressure of the solute are propor-

tional to n/N_1 . (e) Elevation of b. p., and depression of m. p., of the solvent are proportional to $n/(N_1 - n)$, and can be calculated respectively if the latent heats of boiling or melting of solvent are known. (f) When the ratio n/N_1 is the same in different solutions with the same solvent, the substances, of which n denotes gram-mols. per litre (including the solvent), are in diffusion equilibrium, and their mutual diffusion pressure is $0.082NT(n/N_1)$. This diffusion pressure, which has, hitherto, often been confused with osmotic pressure, is of fundamental importance in physical chemistry and physiology.

W. G.

The Dissociation Pressures of some Nitrides. ROLAND EDGAR SLADE and GEOFFREY ISHERWOOD HIGSON (T., 1919, 115, 215—216).

Structure of Crystals in very thin Laminæ. New Experimental Determination of Molecular Dimensions. RENÉ MARCELIN (*Ann. Physique*, 1918, [ix], 10, 189—194).—The method employed in the investigation consists in examining a thin sheet of the substance between crossed nicols side by side with a thin wedge of quartz which is moved until the same colour is obtained with both, and from the indices of refraction of the quartz and the thickness of the wedge at the measured point calculating the thickness of the lamina of substance under investigation. By this method laminæ of mica and *p*-toluidine have been examined, and it is shown that with mica laminæ may be obtained of thickness equal to the diameter of the molecules. With *p*-toluidine laminæ have been obtained which are certainly not thicker than twice the molecular diameter and probably not thicker than a single molecular diameter.

J. F. S.

The Theory of Gels. SAMUEL CLEMENT BRADFORD (*Biochem. J.*, 1918, 12, 351—381. Compare A., 1917, ii, 366).—The low diffusion constant of the natural emulsoids, by retarding the crystallisation of the hot sols, allows the accumulation of a large excess concentration, which, together with their large value of K in von Weimarn's formula, causes gelation on cooling. The small crystallisation velocity is also responsible for the permanency of the gels and the hysteresis of the sols. The viscosity changes in the sols of the natural emulsoids, by heating, are seen to be in conformity with Einstein's formula, since thermal changes cause alterations in the numbers, as well as the size, of the crystallisation centres. Applying von Weimarn's theory to the reversible sol-gel transformation, the conclusion is drawn that gels should comprise two phases, namely, an ultramicroscopic solid phase, bathed in a liquid dispersion medium, from which it has crystallised and which it retains partly by molecular and partly by capillary forces.

Complex organic substances and such as are highly aggregated in solution tend to crystallise as spherites, and this leads to the supposition that the ultimate solid particles of gels are spherites. This

is supported by the fact that by suitable precipitation with alcohol gelatin can be made to assume the form of microscopic spheres.

The liquid adsorbed at the liquid-solid boundary surfaces of gels is under an internal pressure intermediate between those of the solid and of the liquid. This intermediate value of the internal pressure is much greater than that of the free liquid and conditions certain peculiarities in the properties of gels. W. G.

Velocity of Coagulation. H. R. KRUYT and A. E. VAN ARKEL (*Chem. Weekblad*, 1919, **16**, 220—225).—A preliminary note on the measurement of the velocity of coagulation of colloidal solutions. The hydrosol studied is that of selenium prepared by the reduction of selenious acid by means of hydrazine. The concentration of the hydrosol was determined by direct enumeration of the particles under the ultramicroscope, the progress of the coagulation being exhibited by the fall in concentration observed from time to time over a period of thirteen days after the addition of the electrolyte. In presence of potassium chloride solutions of concentration 10 and 20 mg. mol. per litre coagulation of the standard sol was scarcely perceptible; with 40 and 50 mg. per litre coagulation was extremely rapid. The concentration 30 mg. per litre brought about coagulation at a convenient measurable rate. W. S. M.

Forms assumed by Drops and Vortices of a Gelatinising Liquid in Various Coagulating Solutions. EMIL HATSCHKE (*Proc. Roy. Soc.*, 1919, [A], **95**, 303—316).—The effect of allowing a 14% gelatin sol to fall drop by drop into a solution of aluminium sulphate or ferrous sulphate is described, and illustrations of the forms assumed by the gelatin drops are given in the paper. Temperature and the density of the coagulating medium determine to a large extent the form assumed. By dropping a solution containing 10 grams of gelatin and 8 grams of crystallised potassium ferrocyanide into a solution of copper sulphate of suitable density, discs were produced which bear a remarkable resemblance to highly magnified blood corpuscles. The effect of the addition of a large number of substances to the gelatin solution is also described.

J. F. S.

Investigations dealing with the State of Aggregation.
IV. The Flocculation of Colloids with Salts containing Univalent Organic Ions. S. B. SCHRYVER and NITA E. SPER (*Proc. Roy. Soc.*, 1919, [B], **90**, 400—414).—If adsorption of the discharging ion plays the chief part in the flocculation of colloids, it might be expected that those salts the normal solutions of which have the lowest surface tension would exhibit the greatest flocculating capacity. This capacity was investigated for a series of sodium salts of organic acids and of hydrochlorides of organic bases, of which the normal solutions show wide variations in the surface tensions. As a general rule no relationship was shown to exist between surface tension of the solutions and flocculation capacity.

In only one case, that of the mastic sol, did such a relationship exist—the hydrochlorides of those bases the solution of which had lower surface tensions precipitating the mastic in lower concentrations. It is suggested by the authors that two classes of suspenoid should exist, namely, those which owe their charge to an ion derived from a salt from which they are obtained by hydrolysis, as, for example, the chlorine ion in the ferric hydroxide sol obtained by dialysis of ferric chloride solutions, and those which owe their charge to an ion derived by dissociation in a colloid acting as an electrolyte in which the active, rapidly moving ion is held electrostatically in an outer layer to the other more slowly moving colloidal ion. The former class are designated exionic and the latter endionic colloids. Mastic belongs probably to the latter class.

S. B. S.

Equilibria in the Reduction of Oxides by Carbon. ROLAND EDGAR SLADE and GEOFFREY ISHERWOOD HIGSON (T., 1919, 115, 205—214).

Relations between Distribution Ratio, Temperature, and Concentration in System: Water, Ethyl Ether, Succinic Acid. GEORGE SHANNON FORBES and ALBERT SPRAGUE COOLIDGE (*J. Amer. Chem. Soc.*, 1919, 41, 150—167).—The published data on the solubilities and distribution ratios for this system being insufficiently numerous and concordant, a complete set of new determinations has been made. The ethyl ether used was carefully purified, especially from alcohol, a trace of which may be detected by means of the green coloration given with strong sodium hydroxide solution containing a little permanganate; the presence of 1% of ethyl alcohol is found to increase the solubility of ether in water by about 2%, and that of succinic acid in ether by about 20%, the effect on the solubility of the acid in water being much less. The method of analysis used consisted in shaking a mixture of the desired composition in a "pyrex" vessel shaped like a submarine with periscope; as the stopper is in contact with neither the contents of the vessel nor the water of the thermostat, it need not be greased, danger of contamination being thus obviated. The vessel was rocked at such a speed that the air bubble travelled the whole length to and fro, the rocking being stopped for ten minutes and the two layers extracted separately by inclining the vessel first one way and then the other. Special pipettes were used, which did not require greased stoppers and which allowed of the evaporation of the solutions without transference to other vessels.

The compositions of solutions unsaturated with one of the constituents were determined at 15°, 20°, and 25°, and a series of measurements of the distribution ratio was made at each of the three temperatures and at various concentrations of acid.

If s is the mol. fraction of succinic acid (undissociated) in the water layer, and e , w , σ , ω , and ϵ those of ether in the water layer, water in the water layer, succinic acid in the ether layer, water in the ether layer, and ether in the ether layer, respectively, the com-

plete differential of the distribution ratio ($R=s/\sigma$) with respect to temperature is shown to have the form $dR/dt=(b+an)/\sigma(1-am)-s(\beta+av)/\sigma^2(1-\alpha\mu)$, where $\alpha=[\delta\sigma/\delta\omega]_t$, $\beta=[\delta\sigma/dt]_\omega$, $\mu=[\delta\omega/\delta\sigma]_t$, and $\nu=[\delta\omega/\delta t]_\sigma$. The reasoning involved is followed out by means of a solid diagram. Further, an expression is derived for the value of dR/dt between solutions having constant composition of solvent (compare Herz and Kurzer, A., 1910, ii, 399, 1045), the value thus obtained for dR/dt being 0.0257, whereas the expression given above yields the result, $dR/dt=0.0258$.

Succinic acid is not distributed in constant ratio between water and ether; the ratio of activity to concentration in aqueous solution falls with increasing concentration, or, more strictly, this deviation is greater in water than in ether solution, solvation being undoubtedly largely responsible for this phenomenon.

Application of Rothmund and Wilsmore's mutual solubility equation (A., 1902, ii, 447; compare Nernst, A., 1901, ii, 647) to the solubility data at 20° shows that 60 mols. of H_2O furnish 33 molecules of water, which therefore consist almost entirely of $(H_2O)_2$; this result is only an approximate one, but it agrees well with estimates made by other workers using different methods (compare Richards and Palitzsch, this vol., ii, 97). T. H. P.

Influence of Substitution in the Components on the Equilibrium in Binary Solutions. XIV. Binary Solution Equilibria between Pyrogallol and the Aromatic Amines or Acid Amides. ROBERT KREMANN and LUDWIG ZECHNER (*Monatsh.*, 1918, **39**, 777—805. Compare A., 1918, ii, 69; this vol., ii, 54).—Previous results have led the authors to the conclusion that pyrogallol, as a trihydroxyphenol, should be capable of uniting with three molecules of a primary amine unless the close proximity of the hydroxy-groups leads to steric hindrance. The latter is found to be the case, since pyrogallol unites with only two molecules of aniline, *p*-toluidine or β -naphthylamine, and with but one molecule of α -naphthylamine; with the isomeric phenylenediamines, compounds of the type, 2 molecules pyrogallol + 2 molecules diamine, are obtained, whilst with the para-isomeride there is also formed a compound of two molecules of the phenol with one of the diamine. As is to be expected, an equimolecular compound of pyrogallol and benzamide is found to exist, and a similar compound is in all probability formed from acetamide. H. W.

Influence of Substitution in the Components on the Equilibrium in Binary Solutions. XV. The Binary Systems of Benzophenone with Phenols and their Derivatives. ROBERT KREMANN and LUDWIG ZECHNER (*Monatsh.*, 1918, **39**, 807—832).—The affinity of different classes of substances towards phenols generally appears to be weakened by the replacement of the methyl by the phenyl group in the former; the work now described was undertaken with the object of obtaining a direct comparison of acetone and benzophenone in this respect.

Benzophenone forms equimolecular compounds with phenol and α -naphthol, thus resembling acetone; with β -naphthol, the three mononitrophenols, the three dihydroxybenzenes, and pyrogallol, on the other hand, it gives simple eutectics. It therefore appears that the ability of a phenol to form compounds with benzophenone is lessened by the introduction into it of groups which strengthen its electronegative character.

H. W.

Influence of Substitution in the Components on the Equilibrium in Binary Solutions. XVI. The Binary Systems of Benzophenone and certain Amines. ROBERT KREMANN and RUDOLF SCHADINGER (*Monatsh.*, 1918, **39**, 833—838).—The inability of benzophenone to yield compounds with negatively substituted phenols (preceding abstract) might be due merely to steric hindrance or to insufficient difference in the heteropolarity of the components, such that whilst the electronegative carbonyl group can react with amphoteric phenol, it is unable to do so with its electronegative derivatives. In the latter case, it appeared probable that benzophenone would react with amines. Experiment, however, shows that it yields simple eutectics with *p*-toluidine and with α - or β -naphthylamine. The difference in behaviour of benzophenone towards phenol on the one hand and towards negatively substituted phenols on the other must be ascribed to steric hindrance.

H. W.

Velocity of Reaction in the System $2\text{NO} + \text{O}_2$. MAX TRAUTZ (*Zeitsch. Elektrochem.*, 1919, **25**, 4—9).—Polemical between the author and Bodenstein on the method adopted in calculating from the experimental results in connexion with the above-named system (see Bodenstein, A., 1918, ii, 302; Trautz and Dalal, A., 1918, ii, 162).

J. F. S.

Relationship of the Constants of Formation and Hydrolysis of Esters of Symmetrical Dicarboxylic Acids. ANTON SKRABAL (*Monatsh.*, 1918, **39**, 741—763).—A theoretical consideration of the subject and partial review of the literature. The author is led to the following conclusions.

The esterification of a symmetrical dicarboxylic acid and the hydrolysis of its normal ester in the presence of acid lead to an "acid-ester" equilibrium ($2 \text{ acid ester} \rightleftharpoons \text{normal ester} + \text{dicarboxylic acid}$), the constant, K , of which is related to the constant ratios of consecutive hydrolysis and esterification in accordance with the equation $nn' = K$. If, therefore, the acid-ester equilibrium is not appreciably altered by change in temperature and other experimental conditions, nn' must be constant. This is most readily the case when both n and n' are of the order unity, and when, further, $n = n'$. Actually, K is found to be practically independent of the temperature, and its numerical value is frequently 4, hence the simplified constant ratio, $n = n' = 2$. The acid-ester equilibrium is displaced with decreasing acidity, and in consequence the relation-

ship of the constants for alkaline hydrolysis differs from that for acidic hydrolysis.

The esterification of a symmetrical dihydric alcohol and the hydrolysis of its normal ester leads to an "ester-alcohol" equilibrium ($2 \text{ ester alcohol} \rightleftharpoons \text{normal ester} + \text{alcohol}$), the constant, K , of which is related to the constant ratios of the consecutive actions according to the equation $nn' = K$. The "ester-alcohol" equilibrium is not influenced by the acidity, and the relationship of the constants is consequently the same for acid and alkaline hydrolysis.

Replacement of the alkyl group is analogous to esterification and hydrolysis. Consecutive replacement in a symmetrical mixed ester leads to the establishment of a "mixed-ester" equilibrium, the constants of which are similarly related to the ratios of the constants for consecutive replacement. The ratios of the constants of the hydrolysis and formation of mixed esters are governed by their relationships to the constants of the two acid-ester equilibria (or ester-alcohol equilibria) and of the mixed ester equilibrium.

The dynamic conception of the ester equilibrium imposes necessary, but not complete, conditions with respect to the relationship of the constants of formation and hydrolysis of symmetrical diesters and its variation with the experimental conditions. The possible variations are limited by the simultaneous application of the parameter rule (A., 1916, ii, 607). The latter leads to assumptions which can be experimentally tested, and are therefore valuable working hypotheses.

H. W.

Consecutive Reactions. V. Dynamics of the Oxalic Ester Equilibrium. ANTON SKRABAL and DANICA MRAZEK (*Monatsh.*, 1918, **39**, 697—739. Compare A., 1916, ii, 477; 1917, ii, 250; 1918, ii, 12).—The hydrolysis of normal methyl oxalate, the esterification of oxalic acid, and the reaction of the acid ester in aqueous-alcoholic solution have been kinetically investigated at 25°. The acid titre and the amount of normal ester have been analytically determined at given intervals of time. All three processes show uniformly that the relationship of the constants is 2:1 both for the consecutive hydrolysis of the normal ester and for the consecutive esterification of oxalic acid. The esterification equilibrium of oxalic acid has been determined for both stages of the process.

H. W.

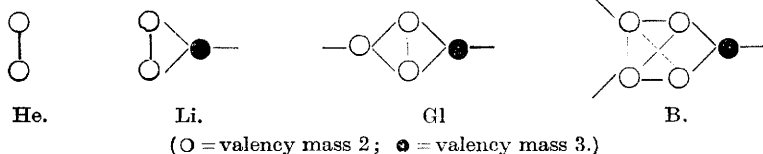
Hydrolysis of Ethyl Oxalate with Alkali. ANTON SKRABAL and ANTON MATIEVIC (*Monatsh.*, 1918, **39**, 765—773).—To gain insight into the influence of the nature of the alkyl group on the velocity of hydrolysis of esters, the authors have examined the behaviour of ethyl oxalate under conditions similar to those used with the methyl ester (A., 1917, ii, 250). Comparison of the constants obtained with those found for the methyl ester shows the latter to undergo the first stage of hydrolysis three times as rapidly, and the second stage two and a-half times as rapidly, as the ethyl ester.

H. W.

Studies in Catalysis. X. The Applicability of the Radiation Hypothesis to Heterogeneous Reactions. WILLIAM CUDMORE MCCULLAGH LEWIS (T., 1919, 115, 182—193).

Chemical Structure of Atoms. I. FRANZ WENZEL (*J. pr. Chem.*, 1918, [ii], 98, 155—203).—A theoretical paper containing the following sections:

I. *Typical Elements*.—The author's method of building structural forms of atoms is based on two hypotheses. The first is that the tervalent nitrogen atom is composed of two nuclei united by a double linking (compare A., 1918, ii, 17); in addition to the three valencies, four others are involved in the double linking, thus $-\bullet = \bullet <$. The second hypothesis is that the mass 14.01 of the nitrogen atom is distributed uniformly over these seven valencies, so that with each valency corresponds a mass of approximately two units, designated valency mass 2. It is assumed, therefore, that to each valency is related a definite mass magnitude. This is usually 2, but in connexion with the atoms of lithium, glucinum, and boron a valency mass 3 must be assumed. Starting, therefore, from the helium atom (composed of two singly linked nuclei) the elements of the first small period can be built up by the systematic addition to both nuclei of the helium atom of valency masses 2 and 3 in numbers increasing from 1 to 7; thus,



carbon, nitrogen, oxygen, and fluorine are represented by similar structures containing 6, 7, 8, and 9 valency masses respectively. Analogous structures can be formed for the elements of the second period, starting from the neon atom. The author claims that these structures, which are not at variance with the physical properties of atoms, are fitted to express the most important chemical properties of the elements and render possible the treatment of general questions, such as variability of valency and the cause of the metallic and metalloid characteristics of elements.

II. *Valency Masses and their Mode of Linking*.—Assuming that the forces which hold together the valency masses in the atomic nucleus can be treated as valency forces, the maximal value of the valency masses 2 and 3 (and also of valency mass 1, from which valency masses 2 and 3 must be assumed to be derived) can be ascertained. By introducing these maximal values of the valency masses into the structural pictures above, structural formulæ are obtained which allow the deduction of many interesting phenomena, such as (a) the existence of a metallic form of the quinquivalent nitrogen atom, on which are founded the ammonium compounds, (b) the variations of the atomic weights from whole numbers, (c) a

structural formula of the hydrogen atom which appears to account for its metallic properties and for the variation of its atomic weight from exactly 1.

III. *Stereoisomerism of Ammonium Compounds*.—The preceding theory of atomic structure leads to the evolution of a model of the nitrogen atom which is in agreement with crystallographic requirements concerning the spatial positions of the atoms in ammonium iodide and in tetramethylammonium iodide. By the help of this model the possibilities of isomerism to be anticipated in ammonium compounds can be derived. These are exceedingly complicated, and of all the nitrogen models hitherto proposed only the pyramidal formula of Bischoff is applicable for the graphic representation of the isomerism of ammonium compounds, and then only if it is amplified by the insertion of a diagonal in the square base. For the explanation of such isomerism chemistry must call in the help of crystallography in a much greater degree than has hitherto been the case. The isomerism of the optically active ammonium compounds requires for its establishment the conception of a binuclear nitrogen atom.

IV. *The Metallic Carbon Atom*.—It is known that one of the valencies of the carbon atom occasionally functions with basic properties (Baeyer's carbonium valency). This necessitates a "metallic" carbon atom, the structure of which includes the grouping characteristic of the atoms of the metals. Such a structure can be derived from that of the metalloid carbon atom. In the latter the valencies are directed tetrahedrally, whilst in the metallic carbon atom the three metalloid valencies lie in a plane to which the metallic valency lies at right angles, a spacial disposition of the valencies of the metallic carbon atom which the author claims is confirmed by the position of the atoms in the crystal lattice of graphite.

C. S.

New Reflux Condenser. JAMES J. BAJDA (*J. Ind. Eng. Chem.*, 1919, 11, 52).—A side-tube, leading from the stem of the condenser just above the flask containing the volatile liquid, conducts the vapours into the top of the condenser jacket, where they enter the condensing coil. The lower part of the latter is formed into a siphon-trap, which delivers the condensed liquid into the flask through a tube extending down the stem of the condenser. A branch tube on the coil just above the trap extends through the top of the condenser jacket.

W. P. S.

An Efficient Laboratory Funnel for Filtering Neutral Liquids, especially the Volatile Organic Solvents. T. B. ALDRICH (*J. Ind. Eng. Chem.*, 1919, 11, 139—140).—In this funnel the filter paper is clamped securely between two plates, so that it cannot lift even when the suction is interrupted; the formation of channels and passages for the liquid and precipitate beneath is thus avoided. The funnel is of aluminium and consists of four parts: (1) a cast hollow cylinder with a small flange at the top and a

heavier one at the bottom, both outside, the lower one being screwed; (2) a plate 1.5 mm. thick perforated with 0.75 mm. holes (3 mm. centre to centre); (3) a ring, threaded on the inside and milled on the outside; (4) a conical lower portion provided with a stem and having a flange at the top threaded on the outside to mesh with the threads on the inside of the ring. After the filter-paper has been introduced the ring is screwed up and holds the other three parts together, rubber rings being inserted to render the joints tight.

T. H. P.

Inorganic Chemistry.

Chemical Reactions at Low Pressures. IV. The Clean-up [complete removal] of Nitrogen by a Heated Molybdenum Filament. IRVING LANGMUIR (*J. Amer. Chem. Soc.*, 1919, **41**, 167—194. Compare A., 1915, ii, 467).—When molybdenum filaments are heated at 2000—2400° K in nitrogen at pressures of 40 bars or less (0.03 mm.), great care being taken to exclude moisture, the filaments lose weight at the same rate as if heated in a vacuum. The nitrogen does not attack the filaments, but disappears at a rate independent of the pressure if the latter exceeds 1 bar; the amount of the nitrogen thus disappearing is much less than the chemical equivalent of the molybdenum evaporated, and the ratio, ϵ , of the number of molecules of nitrogen removed to the number of atoms of molybdenum evaporated in the same time decreases from a maximum of about 0.4 to a minimum of about 0.01 as the temperature of the filament or bulb is raised.

With very minute pressures of water-vapour such as result even in presence of drying agents from failure to “bake out” the bulb, no complete removal of nitrogen occurs, although under such conditions molybdenum will remove carbon monoxide and tungsten will remove either nitrogen or carbon monoxide, the value of ϵ in each of these cases being unity.

The fact that ϵ is independent of the pressure, but dependent on the filament and bulb temperatures, indicates that the reaction occurs in the space around the filament, and that each collision between molybdenum atoms and nitrogen molecules results in combination, at least two products being formed; these are probably a first order compound of the formula NMoN and a second order compound, $\text{Mo}\cdot\text{N}_2$, the proportion between the amounts of these two depending on the relative velocity of the molecules at the moment of collision and on the internal velocity of the nitrogen molecules. The former compound is very stable and cannot be decomposed on the bulb by heating to 360°, its formation being favoured by low relative translational velocity of the colliding molecules and by high

internal or rotational velocity in the nitrogen molecule. All those collisions which do not yield the first order compound give that of the second order, which is so unstable that it decomposes practically completely on striking the bulb, owing to the attractive forces between pairs of molybdenum atoms being much greater than between these and nitrogen molecules.

The deposit which collects on the bulb has the following properties. It is spongy and can easily be rubbed off with the finger on opening the bulb, whereas deposits formed in a high vacuum are dense and can scarcely be scratched off with a knife. If the bulb is kept at the temperature of liquid air, the deposit formed gives up some nitrogen when warmed to the ordinary temperature, but only part of this nitrogen is absorbed again on cooling the bulb; the larger part of the nitrogen in the deposit is not, however, liberated by heating in a vacuum at 360° . The deposit very rapidly absorbs up to about one-thirtieth of its chemical equivalent of nitrogen when cooled by liquid air, but it does not readily absorb hydrogen under these conditions. At the ordinary temperature or above, however, large quantities of hydrogen are absorbed or dissolved by the deposit, these being given up slowly at 300° in a good vacuum. When heated in nitrogen at 270° or above, the deposit combines with nitrogen, and this is not given off again at 360° in a vacuum. The deposit reacts rapidly with water-vapour at the ordinary temperature with production of hydrogen, much of which remains dissolved in the deposit until liberated by heating. T. H. P.

Formation of Ammonia by the Electric Discharge. E. BRINER and A. BAERFUSS (*Helv. Chim. Acta*, 1919, **2**, 95—100).—As the result of experiments on the production of ammonia from nitrogen and hydrogen by means of the electric arc it is found that the yield of ammonia is more than doubled when the ratio of nitrogen to hydrogen is increased from 1:3 to 15:3 by volume. This result, which appears to contradict the rule that the optimum mixture for the formation of a substance corresponds with the composition of that substance, is explained on the ground that at the temperature employed the active participants in the reaction are the atoms, not the molecules, of the two gases and that an excess of nitrogen will be necessary if this gas is more difficultly activated than hydrogen. [See also *J. Soc. Chem. Ind.*, 1919, April.]

C. S.

Combustion of Ammonia in a Deficiency of Oxygen. F. RASCHIG (*Zeitsch. physikal. Chem. Unterr.*, 1918, **31**, 138—142; from *Chem. Zentr.*, 1918, ii, 1016—1017).—It is generally considered that the combustion of ammonia in an excess of oxygen results in the formation of nitric oxide and water; the author considers this view to be erroneous, or, at any rate, not proved. When oxygen is in deficit, reaction is commonly supposed to proceed according to the equation (i) $4\text{NH}_3 + 3\text{O}_2 = 2\text{N}_2 + 6\text{H}_2\text{O}$. Müller (*Zeitsch. physikal. Chem. Unterr.*, 1913, 169) has, however, shown

that under these conditions a quantity of gas is formed containing about 59% nitrogen and 41% hydrogen, and has assumed that a portion of the ammonia dissociates into its constituent elements at the high temperature of the flame. If this were actually the case, considerable quantities of nitrogen should be formed when oxygen is in excess, whereas the yield of nitric acid is actually 90% and over. An explanation may be found in the formation of the hypothetical di-imide when oxygen is in deficit: [(ii) $\text{NH}_3 + \text{O}_2 = \text{N}_2\text{H}_2 + 2\text{H}_2\text{O}$], which would probably decompose into nitrogen and hydrogen. The author has heated potassium hydrazinesulphonate with potassium hydroxide in the expectation that the hydroxyhydrazine primarily formed would immediately pass into di-imide by loss of water; actually, the calculated amount of potassium sulphite was formed and a mixture of equal volumes of nitrogen and hydrogen was evolved. A similar result was obtained by the decomposition of benzenesulphonhydrazide, $\text{NH}_2\cdot\text{NH}\cdot\text{SO}_2\text{Ph}$. Müller's experiments can be interpreted by supposing that the combustion of ammonia takes place partly according to equation (i) and partly with formation of di-imide. It is, however, possible that the first reaction does not occur at all, but that combustion proceeds with intermediate formation of hydrazine [(iii) $4\text{NH}_3 + \text{O}_2 = 2\text{N}_2\text{H}_4 + 2\text{H}_2\text{O}$], which subsequently decomposes into nitrogen and hydrogen. Actually, the author has been able to establish the production of hydrazine (by isolation of benzylazine) when oxygen burns in ammonia. Combustion, therefore, probably proceeds mainly in accordance with equation (ii), and to a less extent according to equation (iii), whilst oxidation in accordance with equation (i) may be considered not to occur at all.

H. W.

Formation of Azoimide by Oxidation of Hydrazine.

A. ANGELI (*Atti R. Accad. Lincei*, 1918, [v], 27, ii, 389—393).—The author's experiments (A., 1894, ii, 93) were carried out in accordance with theoretical considerations which referred to the analogies in behaviour shown by hydrazine, hydroxylamine, and hydrogen peroxide, and were completely confirmed experimentally. Browne and Overman (A., 1916, ii, 245) and Sommer (A., 1917, ii, 30), on the other hand, attempted merely to obtain an explanation of a reaction discovered accidentally by them, namely, the formation of azoimide by oxidation of hydrazine, the only connection with the author's work lying in the fact that, to explain the formation of azoimide from hydrazine some intermediate poly-nitrogenated compound must be assumed. This intermediate term is probably tetrazone, $\text{NH}_2\cdot\text{N}^+\text{N}^-\cdot\text{NH}_2$ (A., 1917, i, 452; compare Willstätter and Pfannenstiehl, A., 1905, i, 723).

T. H. P.

The Oxidation of Nitric Oxide by Dry Air. ANDRÉ SANFOURCHE (*Compt. rend.*, 1919, 168, 307—310. Compare this vol., ii, 105).—A study of the oxidation of nitric oxide by dry air at temperatures ranging from -50° to 525° . The first stage in the oxidation, namely, the conversion of nitric oxide into nitrogen

trioxide, is practically instantaneous and independent of the temperature between the limits given. The next stage, the oxidation of the nitrogen trioxide to nitrogen peroxide, is regulated by the reversible reaction, $2\text{N}_2\text{O}_3 + \text{O}_2 \rightleftharpoons 4\text{NO}_2$, in which the displacement is from left to right up to 200° , but tends more and more towards right to left as the temperature rises from 200° to 525° . W. G.

The Cycle of Oxidation of Nitric Oxide in the Presence of Water. ANDRÉ SANFOURCHE (*Compt. rend.*, 1919, 168, 401—404).—In the presence of water, nitric oxide is oxidised to nitrogen trioxide and not to the peroxide, the trioxide then being decomposed by the water, giving nitric acid and a partial regeneration of nitric oxide. In the presence of nitric acid (D 1.5), however, the nitrogen trioxide is oxidised with the formation of the peroxide and water, according to the equation $2\text{HNO}_3 + \text{N}_2\text{O}_3 = \text{H}_2\text{O} + 2\text{N}_2\text{O}_4$. This oxidation is first noticeable with nitric acid (D 1.3), which has a concentration of approximately 50%, but is not complete, and progresses further as the concentration of the nitric acid used is increased. W. G.

Apparatus [to Demonstrate] the Decomposition of Nitric Acid at a Red Heat. H. BÖTTGER (*Zeitsch. physikal. Chem. Unterr.*, 1918, 31, 152; from *Chem. Zentr.*, 1918, ii, 1005).—The apparatus consists of a small quartz distilling flask provided with a dropping funnel and connected with an inclined condenser and small glass cylinder; the stopper of the latter carries a glass tube leading to a pneumatic trough for the collection of oxygen. Condenser and cylinder are cooled by a freezing mixture. The nitric acid is allowed to drop into the strongly heated flask; a green liquid, consisting of condensed nitrogen peroxide, water, and unchanged nitric acid, collects in the cylinder. H. W.

Electrochemical Preparation of Salts of Perphosphoric Acid and of Monoperphosphoric Acid. FR. FICHTER and ANTONIO RIUS Y MIRÒ (*Helv. Chim. Acta*, 1919, 2, 3—26. Compare Fichter and Müller, A., 1918, ii, 439; Rius y Mirò, this vol., ii, 63).—Most of the work has been already published (*loc. cit.*). The amount of monoperphosphoric acid increases with increasing current density, with decreasing total concentration, and with decreasing alkalinity. If the electrolysis is prolonged to produce high concentrations, the current yield decreases largely. With suitable electrodes, the yield of perphosphate is 64% and of monoperphosphate somewhat more than 7%. These salts are formed in moderate yield even in the absence of fluoride provided the electrolyte is rich in alkali; also both peroxidised salts are obtained by the electrolysis of a mixture of tetrapotassium and dipotassium pyrophosphates. In strongly acid solution, perphosphoric acid decomposes spontaneously in about two days into monoperphosphoric acid and phosphoric acid. Monoperphosphoric acid also decomposes in acid solution, but much more slowly than in alkaline solution. C. S.

Graphitic Carbon. V. KOHLSCHÜTTER (*Zeitsch. anorg. Chem.*, 1919, 105, 35—68).—The physical and chemical properties of graphite vary within such wide limits that no distinct line of demarcation can be drawn between graphite on the one hand and amorphous carbon or soot on the other. From the consideration of a mass of data relating to the properties and mode of occurrence of natural graphite, and the methods of formation and properties of artificial graphite and amorphous carbon, the author comes to the conclusion that all varieties of graphite and amorphous carbon are different physical forms of "black carbon," which is to be regarded as an allotropic modification of diamond. The properties of different samples of graphite depend on the conditions under which it is produced, and its variable character is to be attributed to different degrees of dispersity. The reactions favourable to the production of graphite fall into three groups: (1) surface reactions; (2) reactions *in situ*; (3) surface layer reactions. These are all reactions of the localised type which have been grouped together in a previous paper in the class of "topo-chemical" reactions (this vol., ii, 156). As an example of the first group, the decomposition of acetylene by copper at 400—500° produces graphite as the result of a slow surface reaction, whereas the spontaneous decomposition at a higher temperature in unlimited space produces soot. The formation of graphite by the decomposition of a carbide, as in the Acheson process, is an example of the second group, and another example is the precipitation of graphite from iron-carbon solutions, where in all probability crystals of cementite are first formed, which then decompose, leaving the graphite particles as pseudomorphs of the cementite crystals. As examples of the third group, there are those reversible reactions which lead to graphite formation, such as the decomposition of carbon disulphide. In these cases, temperature is of importance only in so far as it determines the rate at which equilibrium is attained. Contrary to the generally accepted view, temperature and pressure have little influence on graphite formation except in so far as they influence other conditions.

It is probable that all natural graphite has been formed by a localised reaction of one of the above types. It may in some cases have been formed by metamorphosis of organic carbon in contact with igneous rock, more often probably by the decomposition of carbon monoxide in clefts, catalysed by the metallic oxides present.

The view that there is no essential difference between graphite and amorphous carbon is borne out by the work of Debye and Scherrer on the constitution of graphite and amorphous carbon (A., 1917. ii, 437), which showed that both have the same interference effect on X-rays. The conclusion of these authors that in graphite the carbon atoms are arranged hexagonally in plane layers which are superimposed on one another is in agreement with the present author's idea that graphite owes its peculiar properties to its lamellar structure. This type of structure not only accounts for its peculiar physical properties, but also for many chemical

properties, such as its resistance to oxidation and to reagents, and for the fact that its formation is favoured when free carbon is produced by a surface reaction. The difference between the densities and heats of combustion of graphite and amorphous carbon is discussed, and is shown not to be detrimental to the theory that they are essentially the same form of carbon. The formation of graphitic acid by oxidation of graphite and not of amorphous carbon is due to the peculiar structure of the former and not to the existence of a distinct graphite molecule. E. H. R.

Graphitic Carbon and Graphitic Acid. V. KOHLSCHÜTTER and P. HAENNI (*Zeitsch. anorg. Chem.*, 1919, **105**, 121—144).—For the further elucidation of the structure of graphite (preceding abstract), the oxidation of graphite to graphitic acid and the properties of the latter have been studied. Since the properties of the graphitic acid depend on those of the graphite used, in order to obtain results which could be reproduced, the experiments were confined to a specially pure electrically prepared graphite free from ash. The oxidations were carried out with a mixture of potassium chlorate, nitric and sulphuric acids in the cold under fixed conditions. The peculiar oxidising properties of this mixture are due to the fact that it penetrates the whole mass of the graphite; other oxidising agents which do not penetrate the graphite have little action or oxidise it completely to carbon dioxide.

Repeated treatment of the graphitic acid with the oxidising mixture changes its colour from green to brown or yellow, whilst its carbon content gradually diminishes. Thus after one treatment, the graphitic acid has the composition C=59.02%, H=1.91%, O=39.07%, and after five oxidations, C=54.4%, H=2.14%, O=43.46%. The apparently crystalline particles of graphitic acid are not crystals, but pseudomorphs of the original graphite particles. After repeated washing with water, the graphitic acid passes into solution. The colloidal solution can be flocculated by dilute acids, and the precipitated gel is perfectly soluble in water. The differently coloured graphitic acids merely differ in their degree of dispersity, the more lightly coloured products, obtained by repeated oxidation, being more highly disperse. It is not true, as was formerly supposed, that the colour of the graphitic acid depends on the sample of graphite from which it is made.

When heated or treated with reducing agents, graphitic acid is reduced to carbon. Heating experiments have shown that the gases evolved are water, carbon monoxide, and carbon dioxide, the ratio CO/CO₂ being greater the more slowly the heat is applied. The temperature at which the decomposition becomes explosive is also lower the slower the heating, and if the heating is very slow the decomposition may go quietly to completion without explosion. The black, voluminous residue consists of carbon (99.7% C). It has all the properties of soot, but can be compressed into a mass very similar to graphite. When the decomposition of the graphitic

acid by heat takes place under pressure, the graphitic character of the residual carbon is more marked. By decomposing the graphitic acid under sulphuric acid at 160—180°, a residue was obtained having properties intermediate between those of soot and graphite. Treatment of graphitic acid with reducing agents, such as ferrous or stannous salts, gave products with strongly marked graphitic properties, giving graphitic acid again when oxidised. These products, however, were contaminated with adsorbed iron or tin compounds, which were difficult to remove.

The results of these experiments are held to confirm the opinion expressed in the former paper (*loc. cit.*) that graphite is formed when the reaction resulting in the formation of free carbon is spatially confined (topochemical reaction), and that the difference between graphite and amorphous carbon is purely physical, depending on the conditions of formation. The formation of graphitic acid is likewise topochemical in character, the graphitic acid retaining the structure of the original graphite. E. H. R.

Course of Reaction in Explosions of Dilute Carbon Disulphide-Air Mixtures. G. R. STEWART and JOHN S. BURD (*J. Ind. Eng. Chem.*, 1919, **11**, 130—133).—In the combustion of dilute mixtures of carbon disulphide and air, containing from 2·5 to 4% of the former, from 40 to 60% of the carbon disulphide is oxidised according to the equation $\text{CS}_2 + 3\text{O}_2 = \text{CO}_2 + 2\text{SO}_2$; from 25 to 35% follows the reaction $2\text{CS}_2 + 5\text{O}_2 = 2\text{CO} + 4\text{SO}_2$; the remainder, 15 to 30%, is unchanged. Sulphur trioxide does not seem to be formed. With a mixture containing 2·5% of carbon disulphide, the resulting gases contain about 15% of oxygen, 1% of carbon dioxide, usually less than 1% of carbon disulphide and carbon monoxide, and about 4% of sulphur dioxide. [See, further, *J. Soc. Chem. Ind.*, 1919, April.] W. P. S.

Precipitated Amorphous Silica. P. BRAESCO (*Compt. rend.*, 1919, **168**, 343—345).—From a study of the dilatation of precipitated silica, cast into sticks by admixture with 5% of sodium silicate as a paste and subsequently dried and calcined, the author finds that precipitated silica is amorphous provided that it is only heated to about 600°, but that, if it is calcined at a temperature exceeding 1000° it is crystalline and of the same form as cristobalite. W. G.

Nature of the Gas Evolved when Fused Sodium Hydroxide is Dissolved in Water. W. H. SCHRAMM (*Chem. Zeit.*, 1919, **43**, 69—70).—Evolution of gas is sometimes noticed when fused sodium hydroxide is dissolved in water; the greater part of this gas is air contained in the sodium hydroxide, but a small quantity of oxygen, in addition, is also present. For example, 400 grams of fused sodium hydroxide, when dissolved in water free from dissolved gases, yielded 14·45 c.c. of gas containing 28·7% of oxygen. The quantity of oxygen in excess of that due to the air is derived

from the decomposition of an alkali compound of a higher ferric oxide; this compound is present in the sodium hydroxide, and is probably sodium perferfite, $\text{Na}_2\text{O} \cdot \text{Fe}_2\text{O}_4$. [See, further, *J. Soc. Chem. Ind.*, 1919, April.] W. P. S.

Normal and Acid Sulphates of Sodium. PAUL PASCAL and ERO (*Bull. Soc. chim.*, 1919, [iv], **25**, 35—49).—A study of the equilibrium of the ternary mixture, Na_2SO_4 — H_2SO_4 — H_2O , over a temperature range from -30° to 120° . The results confirm the existence of the following anhydrous salts and hydrates: Na_2SO_4 and its hepta- and deca-hydrates; $\text{Na}_2\text{SO}_4, \text{NaHSO}_4$; NaHSO_4 ; $\text{NaHSO}_4, \text{H}_2\text{O}$; $\text{NaHSO}_4, \text{H}_2\text{SO}_4$; $\text{NaHSO}_4, \text{H}_2\text{SO}_4, 1.5\text{H}_2\text{O}$; $2\text{NaHSO}_4, \text{Na}_2\text{SO}_4$.

There was no indication of the formation of the hydrate of the intermediate salt, $\text{Na}_2\text{SO}_4, \text{NaHSO}_4$, or of the hydrate, $\text{Na}_2\text{SO}_4, 2.5—3\text{H}_2\text{O}$.

Determinations were also made of the temperatures of commencement of solidification of solutions of sodium sulphate in different concentrations of sulphuric acid. Anhydrous normal sodium sulphate is only obtained at the higher temperatures and from dilute acid. From results obtained with solutions of sodium hydrogen sulphate it is shown that, in order to crystallise this sulphate, a considerable quantity of acid must be added to the solution, an acidity equal to 65% sulphuric acid being necessary in order to obtain the anhydrous hydrogen sulphate, the acid sulphates of the type $\text{NaHSO}_4, \text{H}_2\text{SO}_4$ only being obtained with an acidity exceeding 80%.

In order to recover some of the acid from sodium hydrogen sulphate, one of two processes may be adopted. At the ordinary temperature a 40—45% solution of the acid sulphate may be prepared and then cooled to -20° , the liquid being sown with a crystal of the decahydrate, $\text{Na}_2\text{SO}_4, 10\text{H}_2\text{O}$. The liquid separates into a solid phase, and a liquid phase containing at the most 30% of sulphuric acid and about 10% Na_2SO_4 . The second method suggested is to prepare a 75% solution of the anhydrous hydrogen sulphate at 100° and cool to the ordinary temperature. The liquid phase obtained contains about 50% of sulphuric acid. [See *J. Soc. Chem. Ind.*, 1919, April.] W. G.

Basic Exchange in Silicates. II. E. RAMANN and A. SPENGLER (*Zeitsch. anorg. Chem.*, 1919, **105**, 81—96).—Experiments have been made on the action of mixed salt solutions on ammonium permutite, prepared by treating sodium permutite with ammonium nitrate. With mixed solutions of potassium and calcium chlorides in equivalent concentrations, the ammonium is completely replaced. The composition of the resulting permutite is independent of the total salt concentration between 0.1 and 3.25*N*. The ratio of the bases in the end-product is generally different from their ratio in the solution, the final permutite containing relatively more of that base of which there is a smaller proportion in the solution. When potassium, ammonium, and, in most cases, sodium are the predom-

ating bases in the solution, the base ratio in the final permutite corresponds with the ion ratio in the solution. When, however, calcium predominates in the solution, the proportion of calcium in the permutite is much smaller than would correspond with its ion proportion in the solution. Calcium chloride solutions do not bring about complete basic exchange with either ammonium, potassium, or sodium permutite. It is concluded that basic exchange in the case of such silicates as permutite is an ion reaction following the general mass action law, but in the case of calcium, and to some extent sodium salts, a disturbing factor, probably of a physical character, comes into play (compare A., 1917, ii, 468).

E. H. R.

Silver Amalgams Rich in Silver. N. PARRAVANO and P. JOVANOVIĆ (*Atti R. Accad. Lincei*, 1918, [v], 27, ii, 411—412; *Gazzetta*, 1919, 49, i, 6—9).—Silver amalgams rich in silver were prepared similarly to the gold amalgams (see this vol., ii, 161). The specific electrical conductivity curve is not continuous, but consists of two distinct branches: the first extends from 0 to about 2% of mercury, and has the form characteristic of solid solutions. The second, from about 2% to 14% of mercury (the highest proportion of mercury attainable by the method of preparation used), is a straight line, this being characteristic of alloys composed of two distinct crystalline individuals; the latter are the saturated mixed crystals with 2% of mercury and, according to Reinders (A., 1906, ii, 219), the compound, Ag_3Hg .

T. H. P.

[Pure] Calcium Hypochlorite to Replace Dakin's Solution. P. MICHAELIS (*Münch. med. Woch.*, 1919, 66, 45).—The Griesheim-Electron works manufacture as "hyporit" an almost pure calcium hypochlorite containing a little calcium chloride and very little lime; it has over 80% of available chlorine, and forms a stable powder which can be compressed into tablets of accurate dosage. It readily dissolves in water to an almost clear, very faintly alkaline solution, which replaces that of Dakin.

G. B.

Yellow Cuprous Oxide. L. MOSER (*Zeitsch. anorg. Chem.*, 1919, 105, 112—120).—The best method for preparing yellow cuprous oxide is by the reduction of a cupric salt by means of hydroxylamine in presence of alkali. It can also be prepared electrolytically, using an alkali sulphate as the electrolyte and an anode of pure copper. When a copper salt is reduced by Fehling's solution the character of the precipitated cuprous oxide depends on the relative proportion of tartrate solution used; when excess of tartrate is used, red, crystalline cuprous oxide is formed, but with little tartrate, the cuprous oxide is yellow and amorphous.

As first precipitated the amorphous cuprous oxide is light yellow in colour and is probably a hydroxide. In absence of air the colour quickly changes to orange or brick-red, probably through loss of water. It can then be dried without further change. The dried

product contains a variable quantity, 2—3%, of water, held probably by adsorption. At high temperatures, above a low red heat, the water is lost and the yellow, amorphous oxide changes into the red, crystalline form. The yellow cuprous oxide is to be regarded as a primary metastable form, the red, crystalline form being the stable one.

E. H. R.

The Carburation of Ceric Oxide. A. DAMIENS (*Ann. Chim.*, 1918, [ix], **10**, 330—352. Compare A., 1918, ii, 442).—The author shows that the product described by Sterba (compare A., 1902, ii, 399) as an oxycarbide of cerium, $\text{CeC}_2\cdot 2\text{CeO}_2$, is not a definite compound at all. The formation of cerium carbide, CeC_2 , in an electric furnace takes place in three stages: $2\text{CeO}_2 + \text{C} = \text{Ce}_2\text{O}_3 + \text{CO}$, $\text{Ce}_2\text{O}_3 + 9\text{C} = 2\text{CeC}_3 + 3\text{CO}$, $\text{CeC}_3 = \text{CeC}_2 + \text{C}$. The carbide, CeC_3 , is soluble in the cerous oxide, and the intermediate products obtained in the carburation are really solid solutions of this nature, their content of the carbide, CeC_3 , varying with the intensity of carburation. This higher carbide in its turn decomposes, giving the known carbide, CeC_2 , and graphite, thus accounting for the fact that a pure carbide has never been obtained.

W. G.

Disperse Aluminium Hydroxide. I. V. KOHLSCHÜTTER (*Zeitsch. anorg. Chem.*, 1919, **105**, 1—25).—The physical form of any solid substance appearing as the result of a chemical reaction is influenced by the many variable factors which collectively determine the conditions operative at the time of its formation. In particular is this the case when the sphere within which the reaction can take place is limited or localised, as where a solid is formed by a reaction between a second solid and a liquid or gas, the reaction being localised at the surface of the solid. The author's work on the different forms of silver and arsenic (A., 1913, ii, 589, 953) demonstrated the dependence of the physical form of the product on that of the starting material. It is suggested that such strictly localised processes as those here cited should be termed "topochemical" reactions. The study of such reactions is important in connexion with the chemical and physiological processes in plants and animals, and for the study of mineral morphology.

As a noteworthy example of a topochemical reaction, the author has studied the formation of pseudomorphs of aluminium hydroxide by the action of ammonia solution on crystals of aluminium sulphate or ammonium alum. When crystals of either of these salts are immersed in ammonia solutions (1—10*N*), more or less perfect pseudomorphs of the original crystals in aluminium hydroxide are formed, the change being quite rapid and complete. The pseudomorphs can be dried, and sometimes even ignited, without losing their form. The physical characteristics of the pseudomorphs vary very considerably with the reaction conditions, depending especially on the ammonia concentration, temperature, nature of the original crystals, and the nature of the salts present in the reacting solution. For the experiments, crystal particles of graduated sizes were used,

and in order to characterise the resulting pseudomorphs, the average size of the particles was measured after drying at 40°, 110°, and at dehydrating temperature. The pseudomorphs were always smaller than the original crystals, the shrinkage being greater when stronger ammonia solutions were used. The density of the pseudomorphs was always greater from alum than from aluminium sulphate, other conditions being the same. The presence of other salts in the reacting liquor, such as ammonium sulphate, chloride, nitrate, and carbonate, had a considerable influence on the character of the product. The denser pseudomorphs were generally more transparent than the lighter ones.

The pseudomorphs are undoubtedly true gels. After drying at 40° they are rapidly peptised by dilute hydrochloric acid, but after drying at 110° peptisation is slower. The character of the sol obtained varies with that of the pseudomorphs in the same way as their density. The peptisation experiments indicate that the degree of dispersity is greatest in the densest pseudomorphs. The mechanism of the formation of the pseudomorphs and of their peptisation is discussed, the latter being considered a chemical reaction between the hydroxide and acid, as suggested in a previous paper (A., 1916, ii, 485). E. H. R.

The Behaviour of some Alkali Aluminosilicates at High Temperatures. H. LEITMEIER (*Zeitsch. anorg. Chem.*, 1919, 105, 69—80).—The work here described was undertaken to ascertain whether alkali-aluminosilicates, by heating for some time at a temperature just below their melting point, undergo decomposition with loss of alkali to such an extent that the accuracy of the melting-point determination would be affected. Two minerals were examined, a very pure form of orthoclase, adularia, m. p. $1145 \pm 5^\circ$, and the sodium aluminosilicate, labradorite, m. p. $1245\text{--}1250^\circ$. Samples of each mineral were kept upwards of 500 hours at a temperature 10° below the melting point. A small and gradually increasing loss of weight was always observed, of the order of about 0.2%. The loss of weight is attributed to loss of alkali, but is too small to confirm by direct alkali estimation. E. H. R.

Purification by Sublimation, and Analysis, of Gallium Chloride. THEODORE W. RICHARDS, W. M. CRAIG, and J. SAMESHIMA (*J. Amer. Chem. Soc.*, 1919, 41, 131—132).—The method here described for the purification of gallium salts is based on the fact that gallium trichloride sublimes and distils at a low temperature, whereas other chlorides likely to be associated therewith are much less volatile. In the apparatus used, gallium could be burnt in pure, dry chlorine, and the impure gallium trichloride thus obtained distilled in pure chlorine, in nitrogen, and in a vacuum successively; the parts of the apparatus were fused together, so that rubber connexions and ground joints were avoided. Distillation in nitrogen or in a vacuum was found necessary to eliminate dissolved chlorine. The resulting product showed no trace of any other substance in its

spark spectrum when examined in a Hilger wave-length spectrometer. In the best of three preliminary experiments, 0.43947 gram of gallium chloride yielded 1.07087 gram of silver chloride, having required 0.80587 gram of silver for complete precipitation; the values of the atomic weight of gallium calculated from these two data are 70.09 and 70.11 respectively; the determination is to be repeated with larger quantities of the gallium chloride.

T. H. P.

Purification of Gallium by Electrolysis, and the Compressibility and Density of Gallium. THEODORE W. RICHARDS and SYLVESTER BOYER (*J. Amer. Chem. Soc.*, 1919, **41**, 133—134).—The separation of gallium from indium by a method based on the different solubilities of the hydroxides of the two metals in alkali hydroxide solution is incomplete, the gallium thus obtained always containing several per cent. of indium and never showing a higher melting point than 26.9°. Electrolysis in slightly acid solution of a salt of the gallium partly purified by the above process (compare Dennis and Bridgman, A., 1918, ii, 456) yields far better results, the melting point of the gallium deposited being 30.8°, which is higher than any value yet given in the literature.

The compressibility of solid gallium is found to be 2.09×10^{-6} , this value falling exactly on the curve representing compressibility as a periodic function of the atomic weight; gallium containing several per cent. of indium, as obtained by the hydroxide process, gives an appreciably lower value. For liquid gallium, the compressibility is 3.97×10^{-6} , a value almost exactly identical with that of mercury and nearly twice as great as that of solid gallium, although its specific volume is less. This result is in agreement with the universal law that solids have compressibilities distinctly less than those of the same substances as liquids, quite irrespective of their specific volumes.

The densities of solid and liquid gallium are 5.885 and 6.081 respectively.

T. H. P.

Influence of Different Factors on the Critical Velocity of Tempering of Carbon Steels. A. PORTEVIN (*Compt. rend.*, 1919, **168**, 346—348. Compare A., 1917, ii, 372).—From a study of the time of tempering as a function of the diameter of homothetic cylinders, and of the hardness as a function either of the time of cooling or of the diameter of the cylinders, it is shown that, for a carbon-steel containing C=1.07%, Mn=0.08%, the ratio τ , time of cooling, to the diameter is given graphically by two straight lines, differing according as the diameter is above 14 mm. or below 13 mm., and at the same time the hardness undergoes a change of about 200 Brinell units. These two phenomena are the consequence of the sudden lowering of the temperature of transformation with cooling and of the change in the microstructure. The critical velocity of tempering, or, more exactly, the region of velocities of cooling in which this sudden change of phenomena occurs, appears to be the most characteristic property of steel in so

far as its tempering is concerned. The critical velocity is also influenced, notably by the manganese content of the steel, decreasing with it. The minimum temperature of hard tempering is a function of the velocity of cooling, and is lower as the velocity is higher.

Chevenard's results, using a steel wire 0.32 mm. in diameter (A., 1917, ii, 414), when compared with the author's results on a cylinder 20 mm. in diameter, made of steel of almost the same carbon and manganese content, lend support to the view that pressure plays an important part in the formation of troostite. W. G.

Some Mixed Crystals of Calcium Ferrite and Aluminate.

EDWARD D. CAMPBELL (*J. Ind. Eng. Chem.*, 1919, **11**, 116—120. Compare *ibid.*, 1913, **5**, 627; 1915, **7**, 835; A., 1914, ii, 772).—Cooling curve and micrographic investigations have been carried out in order to ascertain (1) if a calcium ferrite of the composition $5\text{CaO} \cdot 3\text{Fe}_2\text{O}_3$ really exists (compare Shepherd, Rankin, and Wright, A., 1911, ii, 725; Rankin and Wright, A., 1915, ii, 50; Sosman and Merwin, A., 1916, ii, 618), and (2) what is formed when a mixture of calcium oxide, ferric oxide, and alumina is melted and then cooled slowly enough to permit the material to be nearly in equilibrium during the entire cooling period. The results obtained confirm the statement that dicalcium ferrite, $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$, and monocalcium ferrite, $\text{CaO} \cdot \text{Fe}_2\text{O}_3$, are the only definite compounds of lime and ferric oxide. Pure tricalcium aluminate, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, may be recovered by crystallisation from a solution of lime in the compound, $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$, as a solvent provided that the concentration of the lime at the beginning of the crystallisation is less than is required to form tricalcium aluminate with all the alumina present. If a solution with the empirical formula $8\text{CaO} \cdot 3\text{R}_2\text{O}_3$, containing ferric oxide and alumina in the molecular proportion 1:3, is slowly cooled, mixed crystals with the ferric oxide and alumina in the ratio 1:7 crystallise out until the ratio $\text{Fe}_2\text{O}_3 : \text{Al}_2\text{O}_3$ in the solution has been increased to 3:5; mixed crystals in the latter ratio then crystallise out, further increase in the $\text{Fe}_2\text{O}_3 : \text{Al}_2\text{O}_3$ ratio being produced until, at about 1370° , the ratio reaches the value 1:1. Those aluminates in which part of the alumina is replaced by ferric oxide are capable of holding in solution less calcium oxide than the pure aluminates. T. H. P.

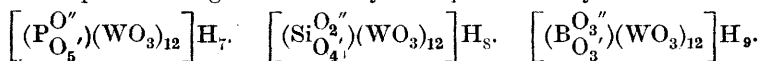
A New Method of Determining the Allotropic Transformation of Nickel. ERNST JÄNECKE (*Zeitsch. angew. Chem.*, 1918, **31**, i, 229; *Zeitsch. Elektrochem.*, 1919, **25**, 9—17).—Allotropic changes in metals are accompanied by a change in the rate of expansion, which, however, is so small that it is difficult to detect. The following method allows the change to be observed over short as well as long intervals of time. A nickel cylinder, 45 cm. long, is inserted in a low-pressure press (3000 kilos.) used for textile and compressive strength tests, and heated by means of a resistance furnace. The variation in length produces a movement of the upper movable plate of the press, which can be registered; move-

ments as small as 0.007 mm. are indicated. The transformation temperature of nickel is 347—360°; the expansion graph consists of two straight lines, that above the transformation temperature being the more steeply inclined.

W. R. S.

Molecular Compounds with High Co-ordination Numbers and with Atomic Groups as Co-ordination Centres. The Stereochemistry of Inorganic Boron, Silicon, and Phosphorus Compounds. PAUL PFEIFFER (*Zeitsch. anorg. Chem.*, 1919, 105, 26—34).—The type of crystal structure which has been revealed by the study of crystals by means of X-rays can be explained chemically on the assumption that the crystal is a complex molecular compound of the co-ordinated type. It is necessary, however, to assume that not only atoms, but also groups of atoms, may function as co-ordination centres, and that co-ordination numbers as high as 8 or 12 are possible. The distribution of the co-ordinated groups around the central atom or group can be represented by reference to a cube. When the co-ordination number is 4, the co-ordinated groups occupy alternate corners of the cube (tetrahedral grouping); six similar groups occupy face centres (octahedral grouping); eight groups occupy all cube corners (cubic grouping), and twelve groups are situated at the centres of cube edges (cubo-octahedral grouping). The author proceeds to show that a number of known compounds may be represented as co-ordinated compounds with co-ordination numbers 8 or 12. Among the former are included compounds of the type $[\text{Mg}(\text{OH}_2)_8]\text{Cl}_2$, $[\text{Mg}(\text{OH}_2)_8]\text{BiCl}_5$, $[\text{Al}(\text{OH}_2)_8]_2(\text{SO}_4)_3$, $[\text{Ca}(\text{NH}_3)_8]\text{Cl}_2$, and the well-known series of double nitrates of the rare earths of the type $[\text{M}''(\text{OH}_2)_8]_3[\text{M}'''(\text{NO}_3)_6]_2$. A number of double fluorides, cyanides, and oxalates are also included.

The alloys of the type NaZn_{12} , KHg_{12} are typical molecular compounds of the 12-co-ordinated type, and should have the same crystalline structure as the metals copper, silver, and gold. The alums can also belong to this type, $[\text{M}'''(\text{OH}_2)_{12}](\text{SO}_4)_2\text{M}'$, and also a number of dodecahydrates of metallic salts. Specially interesting in this connexion are the phospho-, silico-, and boron-tungstates described by Rosenheim and Jänecke (*A.*, 1918, ii, 77). The respective tungstic acids may be represented by the formulæ:



In these formulæ, the central atom (P, Si, B) has six co-ordinated oxygen atoms, and the group (RO_6) itself functions as a co-ordination centre with twelve co-ordinated (WO_3) groups. In the group (RO_6) it is necessary to distinguish two kinds of oxygen atoms in order to account for the number of ionised hydrogen atoms in the molecule. This distinction brings in the possibility of the existence of isomerides, since the groups $(\text{Si}_{\text{O}_4}^{\text{O}_2''})$ and $(\text{B}_{\text{O}_3}^{\text{O}_3''})$ when given an octahedral space configuration can have both *cis* and *trans* forms. These considerations are in perfect agreement with

the facts, for both silicotungstates and borotungstates of this type are known in two forms, whereas no isomerism has been observed in the case of the phosphotungstates. E. H. R.

Investigation by means of X-rays of the Crystal Structure of White and Grey Tin. A. J. BIJL and N. H. KOLKMEIJER (*Proc. K. Akad. Amsterdam*, 1919, **21**, 494—500, 501—504).—From the photographs of white and grey tin previously obtained (this vol., ii, 108), the crystal structures of the two forms have been deduced. T. H. P.

Gold Amalgams Rich in Gold. N. PARRAVANO and P. JOVANOVIĆ (*Atti R. Accad. Lincei*, 1918, [v], **27**, ii, 364—368; *Gazzetta*, 1919, **49**, i, 1—6. Compare this vol., ii, 69, 155).—Previous investigations by various authors lead to the conclusion that in gold amalgams containing between about 90% and 100% of gold, mercury exists dissolved in the gold to form solid solutions. In order more clearly to define the nature of these gold amalgams rich in gold, the authors have measured the electrical resistances at 25° of pure gold and of a series of twenty-one of the amalgams containing from 0.4859% to 9.593% of mercury. These amalgams were prepared by coating gold wire about 0.5 mm. in diameter electrolytically with mercury, heating the wire at 200° for two to three hours, then coating again with mercury and heating, this procedure being continued until the resulting amalgam assumed the desired composition. The homogeneity in composition of the amalgamated wires was demonstrated by microscopic examination and also by analysis. The specific conductivities of the different amalgams are given in the forms of a table and a curve, the latter showing a continuous diminution in the conductivity of gold by increasing proportions of mercury. This behaviour is characteristic for solid solutions. T. H. P.

Action of Alkalis on Crucibles made of Alloys of Platinum or of Gold. PAUL NICOLARDOT and CLAUDE CHATELOT (*Bull. Soc. chim.*, 1919, [iv], **25**, 4—9).—Platinum crucibles undergo marked corrosion when sodium hydroxide or potassium hydroxide is fused in them, and the crucibles are subsequently washed, first with water and then with dilute acid. New crucibles resist better than old crucibles, and the presence of iridium rather diminishes the resistance to corrosion. Potassium hydroxide is decidedly more corrosive than sodium hydroxide. In the case of crucibles of alloys of gold, those made from gold-palladium alloys were the most resistant to the fused alkali hydroxides, but even this alloy was very seriously attacked by sodium peroxide at the concentration necessary for the decomposition of minerals such as chromite. Barium oxide at 825° is much less corrosive than the alkali hydroxides. W. G.

Mineralogical Chemistry.

Volcanic Explosions. I. Explosive Eruptions and their Phases. Combustion of Hydrogen. VENTURINO SABATINI (*Atti R. Accad. Lincei*, 1918, [v], 27, ii, 360—364).—Water-vapour alone is capable of explaining the mechanical effects produced in volcanoes and the projections from the latter, and there is evidence indicating that water-vapour constitutes almost the whole of the gaseous products of volcanic smoke columns; the source of this vapour is not yet established. At the high temperatures prevailing in the depths of volcanoes, the water-vapour is easily decomposable by various elements, with liberation of hydrogen; actual dissociation of the water-vapour to any large extent is improbable owing to the high pressures existing.

The presence of water in the lava may be derived from water of infiltration meeting the very hot lava and being absorbed and decomposed by it, the hydrogen and any residual uncombined oxygen passing up into the crater and there meeting the atmospheric oxygen entering through the fissures, and thus giving rise to violent explosion. The law connecting pressure and temperature inside the laval mass is not known, but it is probable that the latter does not increase at the same rate as the former. At the high temperatures prevailing at great depths, the hydrogen remains gaseous, and at 2000° reaches its maximal density (co-volume).

Laboratory experiments show that the minerals formed at the highest temperatures are spinels, melting at 1900°, whilst iron chromate melts at 1850°, quartz at 1775°, and peridotites at 1730° or above; others generally melt below 1700°. Thus at 2000° or, under high pressures, at a considerably lower temperature lava cannot contain elements in the solid condition. T. H. P.

Volcanic Explosions. II. Calculations on the Combustion of Hydrogen. Comparison with Ordinary Explosives. VENTURINO SABATINI (*Atti R. Accad. Lincei*, 1918, [v], 27, ii, 405—407. Compare preceding abstract).—The energy developed in the explosion of one-ninth of a kilogram of hydrogen, with a co-volume of 1240 litres, is considered, and it is shown that 800,000 kilogram-metres remain available for rupturing the cup of the crater, for enlarging the latter, and for projecting matter therefrom, a loss of one-third of the energy in heat effect and in secondary shocks being assumed. With glyceryl nitrate and explosive gelatin, the corresponding amounts of energy given per kilogram are 625,000 and 652,000 kilogram-metres respectively. T. H. P.

Mimetite, Thaumasite, and Wavellite. E. T. WHERRY (*Proc. U.S. Nat. Mus.*, 1918, 54, 373—381).—Colourless, acicular crystals from the Tintic district, Utah, were thought to be penfield-

ite until it was observed that they had different optical constants ($\omega=2.14$, $\epsilon=2.13$). An analysis made on 6 mg. proves them to be mimetite: PbO 73.3, Cl 2.5, As₂O₅ [24.7] %.

Crystals of thaumasite are described from West Paterson, New Jersey. Although minute, these give the axial ratio $a:c=1:0.931\pm0.003$, and several new forms. Thaumasite is described chemically as "di-hydroxy-tricalcium carbonato-silico-sulphate crystallising with 14H₂O in the hexagonal system."

Wavellite, as divergent groups of minute, acicular crystals in ferruginous sandstone from Hellertown, Pennsylvania, gives the new axial ratio $a:b:c=0.564:1:0.404$. Analysis by F. WYNKOOP agrees with the formula $(Al[OH,F])_3(PO_4)_2+5H_2O$ of Groth, rather than with that of Dana:

Al ₂ O ₃	P ₂ O ₅	SiO ₂	F.	H ₂ O.	Total.	Sp. gr.
36.5	33.4	1.1	0.8+	28.6	100.1	2.325

L. J. S.

Connexion between the Optical Constants and Chemical Composition of the Scapolites.

N. SUNDIUS (*Bull. Geol. Inst. Univ. Upsala*, 1916, 15, 1—12).—The following determinations support the statement of Borgström (A., 1915, ii, 836) that in the minerals of the scapolite group the refractive indices and the double refraction increase with the percentage of carbon dioxide present. I, small, yellow grains with pyroxene from Hesselkulla, Sweden. II, fine-grained, crystalline material with calcite, pyroxene, etc., from Waldviertel, Lower Austria. III, white, fine-grained with little muscovite and calcite, from Froland, Arendal, Norway. IV—VI, from Vahäive, Pahtosvaara, and Kalpivaara respectively, all in the Kiruna district, Swedish Lapland:

	Chloride-marialite.	Sulphate-marialite.	Carbonate-marialite.	Sulphate-meionite.	Carbonate-meionite.	ω	ϵ	$\omega-\epsilon$.
I.	3	—	27	—	70%	1.5880	1.5534	0.0346*
II.	4	—	36	—	60	1.583	1.549	0.035
III.	71	2	—	—	27	1.5516	1.5427	0.012
IV.	36	6	—	—	58	1.575	1.550	0.025
V.	71	—	—	6	23	1.554	1.541	0.0134
VI.	75.5	—	—	3	21.5	1.550	1.540	0.0101

* I, sodium-light; II—VI, daylight.

	SiO ₂ .	Al ₂ O ₃ .	CaO.	Na ₂ O.	Cl.	SO ₃ .	CO ₂ .	H ₂ O.	Total.	Sp.gr.
I.	45.53	28.41	17.49	n.d.	0.10	0.04	4.61	n.d.	96.18	2.730
II.	48.60	27.07	15.69	n.d.	0.17	0.02	4.48	0.23	96.26	2.710
III.	56.82	22.14	7.51	7.64	2.89	0.22	1.14	1.08	100.12*	—

* Incl. K₂O, 0.72.

L. J. S.

Composition of Tourmaline from Utö, Sweden. H.J. SJÖGREN (*Bull. Geol. Inst. Univ. Upsala*, 1916, **15**, 317—324).—The occurrence of tourmaline of different colours in the lithia-bearing pegmatite veins of the Island of Utö, near Stockholm, has long been known. Analyses by N. Sahlbom are of I, the pink variety ("rubellite"); II, pale green; III, greyish-white, nearly colourless; IV, bluish-black. The first three are alkali-tourmalines, and the last an iron-tourmaline. Details are given of the method of analysis. Some of the iron is perhaps present in the ferric state, especially in IV. The results agree closely with the general formula, $H_{20}B_2Si_4O_{21}$, of Penfield and Foote (A., 1899, ii, 304):

	SiO ₂ .	B ₂ O ₃ .	Al ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.	K ₂ O.	Na ₂ O.	Li ₂ O.	P ₂ O ₅ .
I.	36.70	10.76	42.99	1.35	0.28	0.60	0.10	0.49	3.36	0.89	nil.
II.	36.48	9.74	40.03	3.51	0.40	trace	0.08	0.86	2.99	1.11	0.17
III.	36.33	9.79	40.99	1.35	0.37	0.95	0.16	0.50	3.04	1.31	nil.
IV.	35.40	10.45	34.69	9.04	0.41	1.08	0.89	0.60	3.15	0.72	0.13

	F.	H ₂ O < 105°.	H ₂ O > 105°.	Total less O for F.
I.	0.19	0.24	2.75	100.62
II.	0.40	0.17	3.85	99.64
III.	0.39	0.45	4.02	99.46
IV.	0.29	0.09	2.64	99.46

L. J. S.

Analyses of Swedish Glauconites. NAIMA SAHLBOM (*Bull. Geol. Inst. Univ. Upsala*, 1916, **15**, 211—212).—Analysis I is of material from coarsely crystalline Silurian limestone at Eriksöre, Öland. The glauconite was separated from the crushed rock by means of an electromagnet and pure grains picked out under a lens. The grains are olive-green and sharply angular with rough surfaces. Brown, weathered grains were rejected. The material is slowly decomposed by hot hydrochloric acid. At 100° it loses 1.60% H₂O. II is of material mixed with quartz grains from Schonen. The grains are irregularly rounded, with dull lustre and dark green colour; they more closely resemble the ordinary type of glauconite than I. The material is difficultly attacked by hot hydrochloric acid. It loses 2.7—3% H₂O at 100°:

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	CaO.	MgO.	K ₂ O.
I.	51.35	9.47	16.37	4.75	0.63	3.17	7.34
II.	52.74	12.29	9.35	6.30	0.55	4.05	7.97

	Na ₂ O.	F.	P ₂ O ₅ .	H ₂ O. > 100°.	Total.	Sp. gr.
I.	1.22	—	0.35	4.85	99.50	2.82
II.	0.09	0.13	—	5.93	99.40	2.73

L. J. S.

The Eulysite of Södermanland. JOHN PALMGREN (*Bull. Geol. Inst. Univ. Upsala*, 1917, **14**, 109—228).—Eulysite is a dark, fine-grained olivine-augite-garnet rock occurring as beds in gneiss at Turaberg and several other places in central Sweden. It is

usually classed with the peridotites and sometimes with eclogite; the present author regards it as a crystalline schist. The following minerals were isolated from the rock for optical examination by the Fedorov "universal method." The olivine is a manganfayalite; analysis I is of honey-yellow grains picked out from the crushed rock from Gillinge, and II of the portion soluble in dilute hydrochloric acid of the rock from Tunaberg. Diopside from the Gillinge rock gave III, corresponding with $\text{CaMgSi}_2\text{O}_6$ 19%, $\text{CaFeSi}_2\text{O}_6$ 61%, and $\text{MgFeSi}_2\text{O}_6$ 20%. Iron-anthophyllite (IV) from Tunaberg shows a distinct prismatic amphibole cleavage and straight extinction; birefringence, negative, $\gamma - \alpha = 0.020$, optic axial angle $2V = 89^\circ 6'$. The analysis corresponds with $3\text{FeSiO}_3 + \text{RSiO}_2$, where $\text{R} = \text{Mg, Mn, Ca}$. The mineral is very similar to that from Rockport, Massachusetts (Warren, A., 1904, ii, 45). Analysis V is of hornblende from Gillinge. Grunerite, from Strömskult, Tunaberg, with extinction angle ($c:\gamma$) $= 14.5^\circ$, gave VI, corresponding with $\text{FeSiO}_3 + \text{RSiO}_3$. The relation of this to other monoclinic iron amphiboles is discussed. VII of potash-felspar, mainly microcline with some orthoclase, from Gillinge. Garnets at Tunaberg are represented by almandine (anal.

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	CaO	MgO	K_2O	Na_2O	H_2O	Total	Sp. gr.
I.	28.22	—	—	—	63.20	5.19	0.50	2.32	—	—	—	99.43	4.32
II.	31.62	—	0.46	—	35.12	26.61	1.58	4.39	—	—	—	100.00	—
III.	49.84	—	0.78	0.50	19.85	3.66	6.90	18.42	—	—	0.35	100.30	3.544
IV.	47.46	0.03	0.14	0.34	42.34	3.88	1.05	5.05	—	—	0.07	100.25	3.83
V.	37.30	0.93	12.75	7.18	18.73	1.42	11.46	4.94	2.37	0.96	1.22	99.93*	3.35
VI.	50.79	0.07	0.55	0.84	80.64	5.93	1.42	7.87	—	—	1.87	99.98	3.396
VII.	65.15	—	18.14	0.57	—	trace	0.08	trace	14.08	1.27	0.41	100.19†	2.595
VIII.	37.21	0.02	19.37	2.56	23.48	11.04	5.75	0.58	—	—	0.15	100.16	4.115
IX.	37.11	0.10	19.68	1.93	7.72	26.45	6.39	0.75	—	—	0.11	100.24	4.09
X.	47.92	—	0.16	0.46	13.78	27.96	6.20	3.58	—	—	0.28	100.34	3.60

* Also F, 0.17.

† Also BaO , 0.49.

VIII) and spessartite (IX); the former is intermediate in composition between typical almandine and spessartite, and is called manganalmandine. Veins in a richly manganiferous eulysite at Tunaberg are filled with a pyroxenic mineral (named *sobralite*), together with manganfayalite and spessartite. In hand-specimens the former is brown with a lilac tinge. Analysis X is of opaque, pale lilac grains, and corresponds with 4MnSiO_3 , 2FeSiO_3 , CaSiO_3 , MgSiO_3 . Optical examination shows it to be triclinic with cleavages in three directions, and to differ from pyroxmangite (Ford and Bradley, A., 1913, ii, 869) in the position of the optic axial plane. Analyses, also by R. Mauzelius, are given of the rock and of the associated iron-ores and limestones.

L. J. S.

Analytical Chemistry.

Ring Formation in Reactions. F. REISS and G. DIESSELHORST (*Chem. Zeit.*, 1919, **43**, 39).—Certain reactions, such as the blue coloration given by nitrates with diphenylamine and sulphuric acid, are characterised by the formation of a ring, preceding the production of a coloured zone. This is due to adhesion between the liquid and the glass of the tube, and the greater the surface of contact the more sensitive is the reaction. C. A. M.

Use of Filter-paper Pulp in Analysis. O. HACKL (*Chem. Zeit.*, 1919, **43**, 70—71).—The addition of a quantity of filter-paper pulp is advantageous in the filtration of such precipitates as barium sulphate, calcium oxalate, sulphur, ferric hydroxide, aluminium hydroxide, etc., but it should not be used in the last two instances when it is desired to re-dissolve the precipitates in hot hydrochloric acid. A precipitate of ferric hydroxide mixed with filter-paper pulp, when ignited, forms a finely divided powder which dissolves readily in hydrochloric acid. In the case of filtration of silica from a solution containing aluminium salts, the presence of filter-paper pulp retards the rate of filtration. [See, further, *J. Soc. Chem. Ind.*, 1919, 235A.] W. P. S.

The Replacement of Platinum by an Alloy in Apparatus for Electrolytic Analysis. PAUL NICOLARDOT and JEAN BOUDET (*Bull. Soc. chim.*, 1919, [iv], **25**, 84—86. Compare A., 1918, ii, 425).—For the preparation of cathodes, the authors recommend the use of an alloy of gold and copper in the proportion of 9:1 in place of platinum. The total loss in weight of such a cathode, weighing 23.5 grams, was only 0.001 gram during twenty estimations of different types. Anodes may be prepared from the same alloy, but should be coated with a thin layer of platinum electrolytically deposited. W. G.

Apparatus. H. VIGREUX (*Ann. Falsif.*, 1918, **11**, 385—387).—*Apparatus for the Estimation of Ammonia.*—The distillation flask is connected with a vertical fractionating column, the upper part of which is connected with a slightly inclined condensing apparatus. The latter condenses the steam, and the greater part of the condensed water returns through the column into the flask, whilst the ammonia vapours pass to an absorption vessel. *Safety Valve for Water Pumps.*—The valve, which is placed between the pump and the vessel from which the air is to be exhausted, consists of a vertical chamber containing a float; if water flows back from the pump and enters the lower part of the chamber, the float rises and cuts off connexion with the other portions of the apparatus. *Condenser.*—Numerous cross tubes are provided in the inner tube

of an ordinary Liebig condenser; these tubes provide a free passage for the water in the jacket and increase the available condensing surface. [See, further, *J. Soc. Chem. Ind.*, 1919, 200A.]

W. P. S.

Absorption Pipettes. E. VAN ALSTINE (*J. Ind. Eng. Chem.*, 1919, 11, 51—52).—Two vertical cylindrical bulbs, placed one above the other, are connected by a short length of glass tubing, the centre portion of which is constricted to a capillary. A side-tube connects the top of the upper bulb with the tube below the capillary. The bottom of the lower bulb is, by a swan-neck tube, connected with the top of a third bulb, and this, in turn, with a fourth bulb. For use, the absorption solution contained in the fourth bulb is drawn over so as to fill the two cylindrical bulbs; the gas (for example, air containing carbon dioxide) is admitted from the measuring burette into the top of the upper bulb and passes into the lower bulb through the side-tube. Meanwhile, the solution passes gradually through the capillary and continually wets the interior wall of the lower bulb, which now contains most of the gas. Some absorption also takes place in the third bulb, the fourth bulb serving as a reservoir for the solution. [See, further, *J. Soc. Chem. Ind.*, 1919, 201A.]

W. P. S.

Simplified Gas Analysis: Burette without Stopcocks for Gas Analysis. J. J. R. MACLEOD (*J. Lab. and Clin. Med.*, 1918, 4, 69—72; from *Physiol. Abstr.*, 1919, 3, 553—554).—The apparatus is designed for teaching purposes, and is based on that of Haldane. The chief differences are that it has screw clips instead of stopcocks, and a special "pressure adjuster" to adjust the gas pressure in the burette after the screw clips have been tightened.

W. G.

Method for the Extraction and Estimation of Dissolved Gases in Water. F. W. RICHARDSON (*J. Soc. Chem. Ind.*, 1919, 38, 32—33r).—A strong glass bottle of about 1 litre capacity is filled with the water. The lower tube of a bulb or funnel provided with two taps is passed through a rubber stopper, the air is exhausted from the bulb, and the stopper is inserted in the bottle, thereby connecting the tube with the water. When the tap is opened a small quantity of the water enters the bulb, evolution of gas at once begins, and, if the bottle is placed in water at about 40° and the gases removed occasionally from the bulb, the water will continue to boil until all the gases have been expelled and collected.

W. P. S.

Estimation of Chlorate and Perchlorate in Potassium Nitrate. A. WOGGINZ and J. KUBER (*Chem. Zeit.*, 1919, 43, 21—22).—The methods described by Förster (A., 1899, ii, 57), Tschernobéev (A., 1905, ii, 416), Winteler (A., 1898, ii, 90), and Hendrixson (A., 1904, ii, 679) were found to be trustworthy.

W. P. S.

Rapid Method of Estimating Sulphide Sulphur in Pyrites.

A. BARTSCH (*Chem. Zeit.*, 1919, **43**, 33—34).—On heating pyrites with hydrobromic acid in the presence of metallic mercury the whole of the sulphide sulphur is liberated as hydrogen sulphide. Air is expelled from the apparatus, and the last traces of hydrogen sulphide afterwards driven forward by means of a current of carbon dioxide. The hydrogen sulphide is absorbed in an acetic acid solution of cadmium acetate or of zinc acetate and cadmium acetate, and is subsequently estimated by an iodometric method. [See also *J. Soc. Chem. Ind.*, 1919, 171A.] C. A. M.

Estimation of Phosphorus in Vanadium Steels, Ferrovanadium, Non-vanadium Steels, and Pig Iron. CHAS.

MORRIS JOHNSON (*J. Ind. Eng. Chem.*, 1919, **11**, 113—116).—The methods here described make use of a faintly ammoniacal ammonium molybdate solution, which is easy to prepare and convenient to handle, and keeps clear indefinitely. The true phosphorus content of ferrovanadium containing as much as 56.7% of vanadium may be estimated. [See, further, *J. Soc. Chem. Ind.*, 1919, 179A.] T. H. P.

Organic Phosphorus of Soil: Experimental Work on Methods for Extraction and Determination. J. C. SCHOLLEN-

BERGER (*Soil Sci.*, 1918, **6**, 365—395. Compare Potter and Benton, A., 1917, i, 76).—Very full details are given for the estimation of inorganic phosphorus and total phosphorus in the soil, using Neumann's wet combustion for the latter. For the preliminary removal of bases, prior to the extraction of organic phosphorus, it is recommended to wash the soil with 1% hydrochloric acid until 50 c.c. of the extract no longer contains any calcium, after which the acid is washed out by means of a saturated solution of carbon dioxide. The residual soil is then extracted with 4—6% ammonium hydroxide, using 400 grams of soil per litre and shaking two to eight hours, the extract being subsequently filtered through a layer of the soil on a Buchner funnel, this process taking one to three days, and being the most satisfactory for the removal of clay from the extract. Sodium or potassium hydroxide is no more efficient than ammonium hydroxide in extracting organic phosphorus from the soil, and one extraction by the latter alkali, using the proper procedure, removes from the soil practically all the organic phosphorus that is capable of being taken into solution.

No constant relation was observed between total organic matter and organic phosphorus in the ammoniacal extracts, although, as a general rule, they varied in the same direction. For a given soil, it was found that the humus and organic phosphorus in, and the colour of, the ammoniacal extracts, and the total nitrogen content of the soil in the four layers, 0—6 in., 6—12 in., 12—18 in., and 18—24 in., are present in the same relative proportions in each layer.

W. G.

The Estimation of Phosphoric Acid as Ammonium Phosphomolybdate. J. CLARENS (*Bull. Soc. chim.*, 1919, [iv], **25**, 87—90. Compare A., 1918, ii, 128).—A reply to Villiers (compare A., 1918, ii, 333). W. G.

Estimation of Boric Oxide in Glass. J. D. CAUWOOD and T. E. WILSON (*J. Soc. Glass Tech.*, 1918, **20**, 246—252).—Sullivan and Taylor's modification (*Chem. News*, 1915, **111**, 64) of Wherry's method (A., 1910, ii, 92) yields trustworthy results in all cases, whilst Wherry's method itself is untrustworthy when the glass contains much zinc or lead. In the modified method, the sodium carbonate fusion is dissolved in water, the insoluble zinc, lead, etc. carbonates are removed by filtration, and the filtrate then acidified and treated as in Wherry's method. W. P. S.

Micro-elementary Analysis of Organic Substances. J. V. DUBSKY (*Helv. Chim. Acta*, 1919, **2**, 63—75).—A description of the methods of estimating carbon, hydrogen, and nitrogen by micro-analysis. The advantages of a new micro-balance, by P. Hermann, are enumerated. C. S.

Microelementary Analysis of Compounds containing Sulphur, Halogens, and Oxidised Nitrogen. Double Combustion. CH. GRÄNACHER (*Helv. chim. Acta*, 1919, **2**, 76—84).—To avoid obtaining high results in the estimation of carbon in organic compounds containing sulphur and halogens, and particularly in highly nitrated substances, the author employs a layer of lead peroxide 5 cm. in length at the forward end of the combustion tube beyond the silver roll. The lead peroxide must be maintained at a temperature between 170° and 180°, and this is secured by surrounding this portion of the combustion tube with a copper chamber containing boiling aniline.

A "universal tube" suitable for the combustion of any substance obtained in the organic laboratory is one filled from the boat forwards with (1) silver roll, (2) mixture of equal parts of copper oxide and lead chromate, (3) silver roll, and (4) lead peroxide.

Arrangements of apparatus are described whereby the estimation of the nitrogen or of the carbon and the hydrogen in two substances in two tubes side by side can be performed simultaneously. C. S.

The Red Iodotannic Reagent. D. E. TSAKALOTOS and D. DALMAS (*Bull. Soc. chim.*, 1919, [iv], **25**, 80—84).—The sensitiveness of the iodotannic reaction (compare A., 1918, ii, 454) is much greater than that of starch-iodide, especially for very dilute solutions of iodine, but the reaction is interfered with by the presence of potassium iodide, which, on the other hand, increases the sensitiveness of the starch-iodide. An excess of either iodine or tannin inhibits the formation of the red colour in the iodotannic reaction. W. G.

Estimation of Cadmium by the Hydrogen Sulphide Method. EDWARD SCHRAMM (*J. Ind. Eng. Chem.*, 1919, **11**, 110—113).—The literature of the estimation of cadmium and the general considerations governing it are discussed, and a method described which permits of the accurate estimation of cadmium in brass. [See *J. Soc. Chem. Ind.*, 1919, 181A.] T. H. P.

A Very Sensitive Reaction of Copper. Application to the Analysis of Ashes and of Arable Soils. L. MAQUENNE and E. DEMOUSSY (*Compt. rend.*, 1919, **168**, 489—492).—When potassium ferrocyanide is added to a very dilute solution of copper chloride in hydrochloric acid in the presence of a zinc salt so that the copper and zinc are in the proportion of 1:4 or 5, the liquid is first tinged yellowish-red, but gradually a precipitate forms which when separated is seen to be blue. This is a very delicate test for copper in the absence of iron, manganese, or nitric acid, and may be applied to the detection and estimation of traces of copper in plant ashes if the copper is first separated electrolytically. [See *J. Soc. Chem. Ind.*, 1919, 235A.] W. G.

Estimation of Iron in Ores by Permanganate. ROBERT SCHWARZ and BERNHARD ROLFES (*Chem. Zeit.*, 1919, **43**, 51).—In the estimation of ferrous chloride in hydrochloric acid solution a mixture of manganese sulphate and phosphoric acid is added to inhibit the oxidation of the hydrochloric acid by the permanganate. This, however, is not perfectly effective; the results are always high, and hitherto it has been customary to correct this error by standardising the permanganate under the conditions under which it is used in the titration, thereby employing a false standardisation value. The authors have found that colloidal silicic acid exerts a perfect protective action, when used in addition to the manganese sulphate and phosphoric acid mixture, and that correct results are then obtained with permanganate standardised by any of the usual methods. About 4—5 grams of the ore are dissolved in 40—60 c.c. of boiling, strong hydrochloric acid, and the solution made up to 500 c.c. Fifty c.c. of the liquid are reduced with stannous chloride, the excess of the latter removed by mercuric chloride, 10 c.c. of the manganese sulphate and phosphoric reagent are added, and about 5 c.c. of a solution of "water-glass," D 1.17, 1 c.c. of which contains about 0.1 gram of SiO_2 . The silicic acid must not separate in a flocculent condition, but remain in colloidal solution; the titration with permanganate should be made without delay. If the reduction of the iron be effected in another manner and no mercurous chloride be present, the silicic acid alone is capable of inhibiting the oxidation of the hydrochloric acid in the same way as the manganous salt. J. F. B.

The Estimation of Zirconium. PAUL NICOLARDOT and ANTOINE REGLADE (*Compt. rend.*, 1919, **168**, 348—351).—Zirconium is quantitatively precipitated either in neutral solution or in the presence of sulphuric acid, up to 20% of acid, by the addition

of ammonium phosphate, the precipitate being calcined, ignited, and weighed as the pyrophosphate, using the factor 0.487 for converting the weight of pyrophosphate into weight of oxide. This method may be used for the separation of zirconium from iron, chromium, and aluminium. In the presence of iron and chromium an acidity equal to 20% sulphuric acid is necessary to keep up these two metals, but if aluminium is the only other metal present 10% acid is sufficient.

W. G.

A Microchemical Reaction for Gold, Silver, and Rubidium (Cæsium). FRIEDRICH EMICH (*Monatsh.*, 1918, **39**, 775—776).—Blood-red crystals are formed when solutions of gold chloride are brought into contact with silver chloride and rubidium chloride; these can be employed in the detection of the three metallic ions. The place of rubidium may be taken by cæsium and probably by potassium. The new salts appear to be comparable with the well-known triple nitrites, and, like the latter, promise to be useful in micro-analysis.

H. W.

The Estimation of the Methoxyl Group. JOHN THEODORE HEWITT and WILLIAM JACOB JONES (*T.*, 1919, **115**, 193—198).

[**Estimation of Methoxyl Groups.**] M. HÖNIG (*Monatsh.*, 1918, **39**, 871—872).—In a recent communication (Hönig and Spitzer, *A.*, 1918, **i**, 375), a method of estimating methoxy-groups in substances containing sulphur has been described in which the methyl iodide and hydrogen sulphide are absorbed in pyridine containing silver nitrate, and the estimation is completed after removal of the silver sulphide; the procedure was erroneously designated as a modification of the method of Kirpal and Bühn, who, however, employed pure pyridine only. Further details with respect to the accuracy of the new method are promised in a subsequent communication.

H. W.

Estimation of the Geraniol Content of Citronella Oil. A. W. K. DE JONG (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 576—581).—The method for the estimation of geraniol in citronella oil given in Schimmel & Co.'s Bericht (*A.*, 1900, **ii**, 175; 1912, **i**, 880) is based on quantitative esterification of the geraniol by phthalic anhydride, and this the author finds to be impossible of attainment, although with mixtures of geraniol and citronellal this method gives results differing but little from the true values; the amount of citronellal esterified by phthalic anhydride increases with that of the geraniol present. Similarly, the esterification of citronellal by means of acetic anhydride is increased by the presence of either acetic acid or geraniol, but complete esterification is here not possible without the use of sodium acetate.

T. H. P.

Modifications of Benedict's and Folin's Quantitative Sugar Methods. HOWARD D. HASKINS (*J. Biol. Chem.*, 1919, **37**, 303—304).—In using Benedict's method (compare *A.*, 1911,

ii, 340), sodium thiocyanate may replace potassium thiocyanate in preparing the solution if 105 grams of the former salt are used in place of 125 grams of the latter. In Folin's modification (compare A., 1918, ii, 207) of this method, the author recommends for the mixture of salts 20 grams of sodium thiocyanate, 60 grams of anhydrous sodium carbonate, and 100 grams of disodium hydrogen phosphate, using 4 grams of this mixture for each estimation, and boiling for only half the time recommended by Folin. W. G.

Titration of Sugars by Rupp and Lehmann's Method.

E. SCHOWALTER (*Zeitsch. Nahr. Genussm.*, 1918, **36**, 180—187).—This method (A., 1909, ii, 442) yields trustworthy results only when carried out under the exact conditions as to concentration of the solutions, etc., employed in constructing the sugar tables used for reference. In the iodometric titration of the excess of copper, an aliquot portion of the solution should be taken if the amount of unreduced copper is large. [See, further, *J. Soc. Chem. Ind.*, 1919, April.] W. P. S.

Estimation of Soluble Starch in the Presence of Starch and its Hydrolytic Cleavage Products.

JAMES CRAIG SMALL (*J. Amer. Chem. Soc.*, 1919, **41**, 107—112).—The method is based on the insolubility of the blue iodine compound of soluble starch in the presence of a half-saturated solution of ammonium sulphate. Three grams of the sample are dissolved by suspending in 200 c.c. of water and heating to the boiling point. The liquid is made up to 250 c.c., and the unconverted starch removed by filtration or centrifuging; 200 c.c. of the filtrate are then treated with 10 c.c. of a 4% solution of iodine in 6% potassium iodide solution, and an equal volume of saturated ammonium sulphate solution is added. The flocculent precipitate is consolidated in the centrifuge, the clear liquid siphoned off through a filter, and the precipitate is washed about five times by shaking with water, adding an equal volume of saturated ammonium sulphate solution, and centrifuging each time. The washing is continued until the brown coloration due to erythrodextrin has been removed. The blue precipitate in the centrifuge bottle, and any minor portion of it which has been collected on the filter, are washed into a flask with a total volume of water not exceeding 300—400 c.c., and dissolved by boiling, after the addition of 5 c.c. of hydrochloric acid, D 1.125; the iodine is driven off, and the starch is completely saccharified by adding a further 20 c.c. of acid and heating in the boiling water-bath for four hours. The dextrose is determined polarimetrically and calculated as starch. This method gives accurate results, even in the presence of large proportions of dextrins. It is to be noted that the violet iodine compound of amyloextrin is also precipitated by ammonium sulphate if an excess of iodine is present; it is dissolved, however, in the course of the washing, after the excess of iodine has been removed. Amylodextrin may therefore be determined by difference, washing by the above method in the one case,

and with the addition of excess of iodine solution to each wash water in the other. J. F. B.

Glycogen Estimation. I. YAMAKAWA (*Tokyo. Igak. Zasshi*, 1917, **31**, 47—68; from *Physiol. Abstr.*, 1919, **3**, 516).—The tissue is heated with potassium hydroxide at 120°, cooled, neutralised with hydrochloric acid, and then hydrolysed with the same acid. The protein is removed by means of colloidal ferric hydroxide and the dextrose estimated. The removal of the protein is essential, as it acts as a protective colloid. The results obtained in this manner are higher than those by previous methods. W. G.

Simple Method for the Determination of the Digestibility of the Cellulosic Part of Vegetable Fibres, especially of Woody Fibres. P. WAENTIG and W. GIERISCH (*Zeitsch. physiol. Chem.*, 1918, **103**, 87—103).—Recent research on woody matter has shown that thorough removal of the lignified substance from the fibres is necessary in order to obtain material of a moderately high degree of digestibility. The authors have devised a simple method for obtaining rapidly an approximate measure of the non-saccharifiable, and therefore undigestible, material, which interferes with the digestion of the nutrient constituents in woody substances. This method is based on the fact that, when chlorine acts on woody fibre, the lignin is at first almost exclusively attacked, the proportion of lignin present corresponding with that of the chlorine absorbed. By "chlorine number" is understood the percentage increase in weight, calculated on dry matter, occurring when the woody material is subjected under certain definite conditions to the action of a current of moist chlorine. As a general rule, the chlorine number and indigestibility increase or diminish together. [See *J. Soc. Chem. Ind.*, 1919, 195A.] T. H. P.

The Test for Tartrates Depending on the Formation of the Copper Tartrate Complex. L. J. CURTMAN and B. R. HARRIS (*J. Amer. Chem. Soc.*, 1919, **41**, 207).—The statement made by Curtman, Lewis, and Harris (*A.*, 1918, ii, 87) that comparatively small amounts of phosphates or borates, when treated according to Böttger's procedure ("The Principles of Qualitative Analysis," 1906, 159), respond in the same way as tartrates, is now found to be incorrect; neither of these anions, even in amounts as high as 0.5 gram, gives a blue filtrate. T. H. P.

Fat Extraction Apparatus. E. GRIFFITHS-JONES (*Analyst*, 1919, **44**, 45—47).—An extraction flask is attached in the ordinary way by means of a cork to the lower end of a vertical condenser. The material to be extracted is packed into an extraction thimble which is fitted on to the lower end of the condenser tube, the thimble being thus inside the neck of the flask. The vapours of the solvent contained in the flask are conducted through a side-tube which passes just through the cork closing the flask,

and extends upwards and parallel with the condenser to the top of the latter, and then passes down the condenser tube to approximately the level of the water-intake. The condensed solvent falls into the thimble and passes back again into the flask. [See, further, *J. Soc. Chem. Ind.*, 1919, 201A.] W. P. S.

Estimation of "Saccharin" in Tablets. A. BONIS (*Ann. Falsif.*, 1918, 11, 369—372).—Free sodium hydrogen carbonate is estimated in the tablets by titration with *N*/10-sulphuric acid, using methyl-orange as indicator. The quantity of "saccharin" is found by fusing a portion of the sample with a mixture of sodium carbonate and sodium nitrate, and estimating the sulphate formed; the amount of barium sulphate obtained is calculated into sodium "saccharinate." Free "saccharin" may be present, and is estimated by extraction with ether; in this case, the sodium "saccharinate" remains insoluble, and its quantity may be determined by the fusion method mentioned. Lactose, if present, is estimated separately. *p*-Sulphaminobenzoic acid is detected in the tablets by hydrolysing the sample with hydrochloric acid, concentrating the solution to a small volume, and placing it aside for twenty-four hours; the para-acid crystallises out, and may be collected and weighed. [See, further, *J. Soc. Chem. Ind.*, 1919, 198A.] W. P. S.

Analysis of Commercial "Saccharin." II. Detection and Estimation of Impurities. H. DROOP RICHMOND and CHARLES ALFRED HILL (*J. Soc. Chem. Ind.*, 1919, 38, 8—10t. Compare A., 1918, ii, 339, and Procter, T., 1905, 87, 242).—The methods described deal with the following impurities and properties: *Moisture. Mineral matter. p*-Sulphonaminobenzoic acid.—1.5 Grams of "saccharin" are heated with 10 c.c. of 70.5% sulphuric acid so that the liquid boils in as nearly as possible one minute, and then boiled for exactly thirty seconds, the solution being then poured at once into 15 c.c. of distilled water kept cool by immersion of the vessel in cold water; after mixing, the solution is cooled under the tap, seeded with a trace of the para-acid, and placed in ice-water. If present to the extent of 1%, para-acid crystallises out in thirty minutes or less; if 3% is present, the crystals usually begin to separate before seeding on cooling, and when about 10% is present, the acid begins to crystallise in the hot. *o*-Sulphonaminobenzoic acid. *o*-Toluenesulphonamide.—This dissolves in sodium hydrogen carbonate, whilst "saccharin" is insoluble. *Lead. Arsenic. Ammonia. Easily carbonisable organic matter.*—The test of the British, French, and U.S. Pharmacopœias may be replaced by the coloration obtained in the test for para-acid with 70.5% sulphuric acid (see above). *Sweetness. Melting point.*—Pure "saccharin" has m. p. 229°. *French Codex identification test.*—When heated in a test-tube with a small crystal of resorcinol and several drops of concentrated sulphuric acid, "saccharin" gives a liquid at first reddish-yellow and then dark green. Treatment of the cooled liquid with water and supersaturation with

sodium hydroxide gives a liquid showing intense green fluorescence. This test is, however, not characteristic of "saccharin," since the ortho-acid gives the same result, and the amide a moderate fluorescence.

T. H. P.

Microchemical Identification of Stovaine and Cocaine.

DENIGÈS (*Bull. Soc. Pharm., Bordeaux*, 1917; from *Ann. Chim. anal.*, 1919, [ii], 1, 65—66).—The tests described are carried out on a microscope slide, a small drop of the solution being treated with a drop of the reagent. Platinum chloride does not give a precipitate with a 0.5% stovaine hydrochloride solution, but a fine, granular precipitate is obtained with a 1% solution; in the case of cocaine hydrochloride solution of either of the above concentrations, a characteristic, crystalline precipitate is formed. Gold chloride gives a crystalline precipitate with both alkaloids, but the form of the crystals is quite different for the two salts. Picric acid yields a yellow, crystalline precipitate with stovaine hydrochloride, whilst cocaine picrate is amorphous and changes to yellow, liquid droplets when stirred. [See, further, *J. Soc. Chem. Ind.*, 1919, 198A.]

W. P. S.

Estimation of Morphine in Complex Products. III. Opium and Mixtures containing Opium. ALFRED TINGLE (*Amer. J. Pharm.*, 1918, 90, 851—861. Compare this vol., ii, 87, 88).—The presence of resinous matters in opium interferes with the estimation of morphine by the methods described previously (*loc. cit.*); the greater part of these resins may be separated by heating the slightly alkaline solution containing them, together with the morphine, with an excess of salicylic acid. When the mixture is cooled, the resin is precipitated, and may be removed by filtration. The morphine is then precipitated from the filtrate, collected, redissolved, extracted with alcohol-chloroform mixture, and titrated. [See, further, *J. Soc. Chem. Ind.*, 1919, 116A.]

W. P. S.

New Titration Method for the Determination of Uric Acid in Urine. J. LUCIEN MORRIS (*J. Biol. Chem.*, 1919, 37, 231—238).—A slight modification of the method described for the estimation of uric acid in blood (compare A., 1918, ii, 251).

W. G.

[**Detection of Traces of Blood Pigment.**] JOHN ALEXANDER MILROY (*Biochem. J.*, 1918, 12, 327—329).—See this vol., i, 179.

Impurity in Ethyl Ether giving a Blue Coloration with Benzidine. F. WEEHUIZEN (*Pharm. Weekblad*, 1919, 56, 301—303).—Attention is directed to the presence in some samples of ethyl ether used for analytical purposes of an impurity which gives a blue coloration on addition of hydrogen peroxide and benzidine. Pieces of potassium hydroxide kept in the ether for a time are sufficient to remove the impurity.

W. S. M.

The Value of Walker's Method of Estimating Casein in Milk. A. AGRESTINI (*Staz. sper. agr. Ital.*, 1917, **50**, 109—114; from *Chem. Zentr.*, 1918, ii, 866).—Comparisons of the rapid method devised by Walker (A., 1914, ii, 309) with the process of Schlossmann and von Bondzinski show the former to be very convenient, but not completely trustworthy. The amounts of alkali required to produce neutrality in Walker's procedure after addition of formalin are either identical with or very near to those required in the direct titration of the original milk. This result appears to support the view of Bordas and Touplain (A., 1911, ii, 631) that the acidity of fresh milk depends mainly on the casein, and allows an approximate estimation of the latter by simple titration in the presence of phenolphthalein as indicator. H. W.

Vernes' Method (Sero-diagnosis of Syphilis). ROGER DOURIS and ROBERT BRICQ (*Bull. Soc. chim.*, 1918, [iv], **23**, 472—478. Compare Vernes, *Compt. rend.*, 1917, **165**, 769; 1918, **166**, 575; **167**, 383).—Vernes has shown that serum in the presence of an inorganic or organic colloidal suspension causes a periodic precipitation, the rhythm of which differs according as the serum is normal or syphilitic, and that it is possible to prepare a fine organic suspension of a determined stability which will flocculate with a certain dose of syphilitic serum, but not with the same dose of normal serum. The authors give full details for carrying out the test, using red globules from sheep's blood, pig serum, and "perethynol" (an absolute alcoholic extract of dried, powdered, and de-fatted horse-heart muscle), and measuring, not the flocculation, but the hæmolysis colorimetrically. W. G.

Estimation of Acidity and Titratable Nitrogen in Wheat with the Hydrogen Electrode. C. O. SWANSON and E. L. TAGUE (*J. Agric. Res.*, 1919, **16**, 1—15).—Aqueous extracts of wheat were made at 5°, 20°, 40°, and 50°, the mixture being shaken for times varying from five minutes to twenty-four hours. The hydrogen-ion concentration of the extract as measured by the hydrogen electrode is practically independent of the temperature and the duration of the extraction, but the volume of $N/20$ -barium hydroxide solution necessary to add to bring the extract to a definite P_H value increases with the time of shaking, and within certain limits is proportional to it. As the duration increases, the volume of standard alkali required increases up to a limit, which is reached sooner as the temperature of extraction rises. This phenomenon is due to the presence in the extract of substances which only become ionised when an alkali is added.

The amino-nitrogen, as determined by Sørensen's formaldehyde method, is all extracted in two hours at 40°. The amount of phosphorus in the extract made at 20° directly precipitable by magnesia mixture is about one-half of the total phosphorus present, but at 40° practically the whole of the phosphorus is converted into a form which is precipitated by magnesia mixture. W. G.

General and Physical Chemistry.

Matter and Light. Attempt at the Synthesis of Chemical Dynamics.

JEAN PERRIN (*Ann. Physique*, 1919, [ix], **11**, 5—108).—A purely theoretical discussion in which the author endeavours to show that it is possible to develop a coherent theory, which sees in light the cause of chemical reactions, and which elucidates and correlates varied types of phenomena which at first sight seem quite different. According to the theory, dissociation or combination, phosphorescence, radioactivity, change of physical state, all obey one and the same fundamental law, which is connected with the internal structure of the atom.

W. G.

Dispersion of Diamond. L. SILBERSTEIN (*Phil. Mag.*, 1919, [vi], **37**, 396—406).—A mathematical paper in which the conception of electrical interaction of atoms is applied to the refractive properties of diamond, considered as a known assemblage of fixed atomic centres, each containing a single dispersive electron and becoming a doublet in the presence of an external electric field.

J. F. S.

Regularities of the Second Kind in Line Spectra. J. E. PAULSON (*Zeitsch. wiss. Photochem.*, 1918, **18**, 202—208).—The author, following the lead of Kayser, terms regularities between the wave-lengths of the various spectrum lines, regularities of the second kind. The present paper is a theoretical discussion of these regularities, in which it is shown that the magnetic resolution of the lines of a wave-length system does not follow such simple laws as that of the series lines.

J. F. S.

Vacuum Arc Spectra of Various Elements in the Extreme Ultra-violet.

J. C. McLENNAN, D. S. AINSLIE, and D. S. FULLER (*Proc. Roy. Soc.*, 1919, [A], **95**, 316—332. Compare this vol., ii, 125).—A vacuum arc spectrograph is described, together with the method of operation. The vacuum arc spectra of copper, aluminium, zinc, carbon, iron, tin, thallium, lead, nickel, cobalt, and cadmium have been measured down to $\lambda=1400$. The wave-lengths are compared in all cases with values obtained by other observers, and the intensities and frequencies are included in all the tables. In the case of zinc, the lines $\lambda\lambda=2025\cdot5(16)$, $1821\cdot8(3)$, $1589\cdot6(10)$, $1510\cdot4(1)$, $1491\cdot5(1)$, $1486\cdot2(6)$, $1478\cdot5(2)$, $1477\cdot6(4)$, $1457\cdot9(4)$, $1457\cdot5(4)$, $1451\cdot1(4)$, $1445\cdot0(3)$ were measured. The figures in brackets represent the intensities of the lines. For aluminium, the lines $\lambda\lambda=1989\cdot9(14)$, $1935\cdot1(4)$, $1930\cdot4(10)$, $1862\cdot8(32)$, $1854\cdot5(32)$, $1766\cdot6(4)$, $1761\cdot9(10)$, $1724\cdot3(10)$, $1720\cdot7(8)$, $1718\cdot5(4)$, $1670\cdot6(4)$, $1611\cdot8(14)$, and $1605\cdot6(12)$ were measured. In the case of copper, the lines $\lambda\lambda 2037\cdot3(6)$, $2026\cdot2(4)$, $2001\cdot0(4)$,

1979·6(4), 1748·6(4), 1739·7(4), 1721·8(6), 1708·5(4), 1704·9(2), 1693·4(4), 1692·5(1), 1686·7(4), 1684·6(2), 1681·7(1), 1679·1(2), 1674·6(2), 1671·5(2), 1670·1(2), 1651·9(2), 1642·1(8), 1594·2(8) were measured. The thallium arc was produced by placing metallic thallium in iron cups attached to iron poles; the lines measured in this case were $\lambda\lambda$ 1907·8(14), 1891·8(6), 1827·3(2), 1814·2(6), 1792·2(8), 1660·0(6), 1653·8(6), 1561·8(14), 1559·0(16), 1538·5(5), 1508·2(4), 1499·8(6), 1491·0(2), and 1478·0(4). With tin, the lines $\lambda\lambda$ 2152·5(12), 2041·2(2), 1941·0(1), 1899·8(20), 1831·4(6), 1811·2(20), 1756·6(16), 1741·3(1), 1699·5(10), 1489·2(6), 1475·2(15), 1438·3(4), 1437·3(4), 1402·4(4), and 1400·5(4) were observed. The lead arc was produced in the same way as that of thallium; the lines recorded in this case are 2170·5(8), 2060·5(8), 1925·8(2), 1913·7(4), 1904·2(2), 1898·7(2), 1895·5(2), 1821·7(14), 1796·5(10), 1744·2(1), 1741·1(2), 1726·2(10), 1682·5(12), 1671·6(12), 1597·6(3), 1555·8(12), 1511·7(4), 1494·7(1), 1492·7(1), 1434·0(5), and 1431·9. With a carbon arc, the lines $\lambda\lambda$ 2307·5(2), 2298·0(9), 2219·0(2), 2088·5(5), 1930·5(15), 1758·1(9), 1749·7(5), 1656·9(10), 1562·0(9), 1561·2(9), 1560·5(9), 1550·7(2), 1548·5(3), 1482·8(5), 1464·5(6) were recorded. A cobalt arc gave the lines $\lambda\lambda$ 2138·7(4), 2099·3(2), 2061·5(5), 2026·2(7), 1939·5(2), 1929·5(9), 1912·2(3), 1893·8(4), 1861·4(10), 1853·0(10), 1819·8(2), 1740·3(1), 1710·9(2), 1669·9(7). Mild steel electrodes were used for the production of the iron arc; the lines measured are $\lambda\lambda$ 2394·5(5), 2380·2(5), 2360·0(4), 2346·0(4), 2097·5(2), 2078·8(4), 2061·5(3), 1926·0(2), 1913·8(4), and 1894·3(3). In the case of nickel, forty-one lines lying between λ 2005·0 and λ 1650·1 were measured, but nothing of smaller wavelength than this. With the cadmium arc, the lines observed are $\lambda\lambda$ 1993·5(1), 1988·0(1), 1966·0(1), 1946·0(1), 1940·0(4), 1932·5(4), 1894·5(1), 1874·5(1), 1871·0(1), 1855·5(2), 1846·5(4), 1827·0(1), 1808·0(3), 1790·5(4), 1745·5(2), 1728·0(4), 1711·0(3), 1706·5(2), 1668·5(10), 1656·5(1), 1647·5(2), and 1526·5(1). Reproductions of photographs of the spectrograph and of all the spectra are appended to the paper. J. F. S.

Ultra-violet Light Absorption of Unsaturated Compounds.

H. LEY (*Zeitsch. wiss. Photochem.*, 1918, **18**, 177—191).—The ultra-violet spectra of styrene, α -methylstyrene, β -methylstyrene, stilbene, methylstilbene, α -phenylstilbene, cinnamic acid, β -methylcinnamic acid, and α -phenylcinnamic acid have been investigated. In the case of styrene, a band is found at $1/\lambda = 4100$ ($c = 0.001$, $d = 2$ mm.), and at ($c = 0.01$, $d = 2.5$ — 7.0 mm.) bands occur at $1/\lambda = 3440$ and 3550 . The introduction of a methyl group in the β -position displaces the original continuous absorption and the band 3440 toward longer wave-lengths, whilst the band 3550 vanishes. The introduction of a methyl group in the α -position brings about at higher concentrations a definite displacement toward the ultra-violet, and the absorption between 3400 and 3600 completely disappears. Stilbene possesses a deep band $1/\lambda = 3400$ ($c = 0.001$ and $d = 1$ — 10 mm.); the introduction of a methyl group

into the ethylene group brings about a twofold change in the absorption spectrum: (i) a displacement of the continuous absorption towards the ultra-violet, and (ii) the bands are displaced in the same direction, or, in other words, at the position of maximum absorption the extinction coefficient is smaller. In the case of the derivatives of cinnamic acid, it is shown that β -methylcinnamic acid and α -methylstyrene are optically similar, whilst the same also applies to cinnamic acid and styrene.

J. F. S.

Absorption Spectra of Acid Hæmatin, Oxyhæmoglobin, and Carbon Monoxide Hæmoglobin. A New Hæmoglobinometer. H. S. NEWCOMER (*J. Biol. Chem.*, 1919, 37, 465—496).—

Acid hæmatin has different spectral characteristics under varying conditions as to acid and solvent. The curve for material prepared in the manner described is constant and stable, for several days at least. The prominent band in the red has its deepest point at about 6620 Å.U. The other two bands in the visible spectrum are very shallow. There is a broad, general depression extending from 5100 to 5900 Å.U. which is divided by a very slight rise at 5480 Å.U. The great ultra-violet band of acid hæmatin is broader and shallower than in the case of oxyhæmoglobin, the broadening extending it further into the ultra-violet and obliterating the small peak at 3680 Å.U. which appears in the oxyhæmoglobin curve. There is beyond the peak at 3100 Å.U. a shallow but distinct band with its centre at 2780 Å.U. Beyond 2400 units, the absorption becomes very great. The further side of this band did not appear within the range of the instrument (2050 units). The β -band of oxyhæmoglobin is seen to be fainter than the α -band, but the difference in depth is slight. The great ultra-violet band is much deeper, the ratio of extinction coefficients being about eight. Oxyhæmoglobin has two further bands in the ultra-violet, at 3460 and 2760 Å.U., separated by a peak at 3100, somewhat higher than the corresponding one of acid hæmatin. The similarity in the ultra-violet of the absorption of the two substances would seem to indicate that it is due in large part to a radicle common to both. Carboxyhæmoglobin has an absorption similar to that of oxyhæmoglobin. In the visible, the bands are not so sharp and the transmission is not so great, particularly at the peak between the α - and β -bands. It is the lowness of this peak which accounts for the difference in shade between solutions of the two compounds. The visible bands of carboxyhæmoglobin are approximately of the same depth as the β -band of oxyhæmoglobin; they are shifted with respect to those of oxyhæmoglobin toward the violet; the great ultra-violet band is much deepened and shifted in the contrary direction. In the ultra-violet, the two peaks are higher than in the case of oxyhæmoglobin. The height of the peak at 3760 units and the depth of the band at 4190 units decrease very markedly with loss of CO from solution.

The amount of the extinction due to the admixed serum is only from one-fourth to one-seventh of the whole. The presence of

plasma can be neglected in discussing the visible absorption of these compounds. The blood in the superficial capillaries of the skin would be sufficient in quantity to absorb almost completely all the violet and ultra-violet light which might fall on it.

A "high transmission yellow" semaphore glass has an absorption curve which runs smoothly as a mean through the acid hæmatin curve.

The hæmoglobin value of this glass has been carefully estimated, and by this means a colorimetric method for the determination of hæmoglobin has been elaborated. A colorimeter of the Duboscq type is used.

J. C. D.

A New Sector Spectrometer. SAMUEL JUDD LEWIS (T., 1919, 115, 312—319).

Tyndallmeter for the Examination of Disperse Systems.

RICHARD C. TOLMAN and ELMER B. VLIET (*J. Amer. Chem. Soc.*, 1919, **41**, 297—300).—An instrument is described for measuring the strength of the Tyndall beam in suspensions, colloidal solutions, smoke, and mists. It consists of a 6—8 volt lamp, a condensing lens, and a diaphragm through which the beam of light enters the chamber containing the gas or solution. The strength of the beam is then determined by a Macbeth illuminometer which has been standardised with either a suspension of finely divided silica or an opaque glass.

J. F. S.

Relation between the Intensity of Tyndall Beam and Concentration of Suspensions and Smokes.

R. C. TOLMAN, L. H. REYERSON, E. B. VLIET, R. H. GERKE, and A. P. BROOKS (*J. Amer. Chem. Soc.*, 1919, **41**, 300—303. Compare preceding abstract).—The strength of the Tyndall beam has been determined after passing through silica suspensions and ammonium chloride smokes of various concentrations. It is shown that, in general, for liquid suspensions and smokes there is a strict proportionality between the concentration and the strength of the beam, provided that the concentration does not become high enough to give an opacity which affects the results, and that the size of the particles remains the same throughout the series of measurements.

J. F. S.

Disappearance of Smoke in a Confined Space.

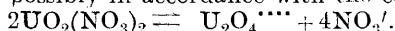
RICHARD C. TOLMAN, E. B. VLIET, W. MCG. PIERCE, and R. H. DOUGHERTY (*J. Amer. Chem. Soc.*, 1919, **41**, 304—312. Compare preceding abstracts).—The gradual disappearance of smokes in confined spaces has been investigated. It is shown that a smoke disappears in an enclosed space owing to coagulation, to settling, and to the diffusion of the particles to the walls, where they adhere. The rate of disappearance was determined by means of a Tyndallmeter in boxes 1 cu. m. capacity with smokes of burning acetanilide, benzoic acid, and resin. The rate of disappearance is markedly increased by

stirring the smoke, owing to the fact that it was brought in contact with the walls, where it adhered. The finer the state of subdivision of the smoke particles, the higher the readings on the Tyndallmeter owing to the greater reflecting surface of the particles. The rate of disappearance of a finely divided smoke of a given concentration is greater than that of a coarse smoke of the same concentration owing to the increased opportunity for coalescence. In smokes of the same size of particles, the rate of disappearance increases with the concentration owing to the increased chances of coagulation and removal by the walls. Since the increased concentration and increased subdivision both lead to a higher rate of disappearance, it is impossible to raise the optical density of a smoke beyond a certain point by the introduction of more smoke material.

J. F. S.

Rotatory Dispersive Power of Organic Compounds. IX. Simple Rotatory Dispersion in the Terpene Series. THOMAS MARTIN LOWRY and HAROLD HELLING ABRAM (T., 1919, 115, 300—311).

Principal Methods for the Determination of the Ionic Constitution of Solutions of Electrolytes and the Application of these to the Solution of Uranyl Nitrate. LÉON GÓMEZ (*Anal. Fis. Quím.*, 1919, 17, 24—49).—A general discussion of the methods adopted to determine the mode of ionisation of an electrolyte in solution. With reference to the solution of uranyl nitrate, the results of the cryoscopic measurements of Dittrich (A., 1899, ii, 629) are examined. It is shown by extrapolation that the apparent molecular weight at infinite dilution is almost exactly one-third of the real molecular weight, so that an ionisation according to the scheme $\text{UO}_2(\text{NO}_3)_2 \rightleftharpoons \text{UO}_2^{++} + 2\text{NO}_3^-$ may be assumed. With increasing concentration, the ratio of the apparent to the real molecular weight approaches the value 2.5, so that even in concentrated solution the salt is ionised to a considerable extent, possibly in accordance with the equation



The values of the degree of dissociation, calculated on the assumption that the salt is a simple ternary electrolyte, are thus uncertain.

Dittrich's measurements of the equivalent conductivity show that up to an equivalent dilution of 4096 litres, the values of Λ do not converge to a limit. By forming the difference between each value of Λ and the next succeeding at double the dilution, it is shown that the difference decreases until the dilution $v=64$ litres is reached. From this point, the difference increases progressively throughout the range of dilution considered. This behaviour is attributed to the progressive ionisation of the salt, according to the equations $\text{UO}_2(\text{NO}_3)_2 \rightleftharpoons [\text{UO}_2(\text{NO}_3)]^+ + \text{NO}_3^-$ and



with subsequent hydrolysis at dilutions beyond $v=64$ litres.

The transport numbers for the anion were determined at concentrations between 0.0024 and 0.074 mol. per litre, the fall in concentration of UO_2 at the anode being measured. The curve obtained resembles that for a typical ternary electrolyte, and shows a minimum at concentration 0.015 mol. per litre, indicating a maximum concentration of $[\text{UO}_2(\text{NO}_3)]$. At concentrations beyond 0.07 mol., the transport number approaches unity, the "metallic" radicle now forming part of the anion. At concentrations lower than 0.01 mol., the presence of UO_2 is indicated.

The addition of ammonia to a uranyl solution precipitated the compound $(\text{NH}_4)_2\text{U}_2\text{O}_7$. This indicates the probable presence of the anion U_2O_7 in the solution.

W. S. M.

Internally Complex Salts and Conjugated Salts of Alkali Metals. II. I. LIFSCHITZ and GEORG BECK (*Helv. Chim. Acta*, 1919, 2, 133—143. Compare A., 1914, ii, 512).—In the earlier communication, it was shown that the alkali salts of oximino-ketones and erythronitrolic acid have much lower electrical conductivities than the salts of simple acids in methyl-alcoholic or acetone solutions. It appeared at first sight that this abnormality was connected with the conjugated structure of the salts, which is superficially analogous to that of internally complex salts of the heavy metals. In the common cases of conjugated salts, no colour change accompanies electrolytic dissociation, and therefore it appeared to be of great interest to determine whether abnormal conductivity, in the above sense, is usual with such salts, as this would furnish a means of recognising conjugated structure. As far as solutions of the salts in methyl alcohol are concerned, it is found that conjugated structure causes no anomalies, which suggests that the peculiarities of the oximino-ketone salts require some other explanation.

The molecular conductivities of the sodium or potassium salts of the following compounds in methyl alcohol are recorded; hydriodic, acetic, propionic, butyric, valeric, benzoic, the three nitrobenzoic, benzenesulphonic, and *p*-phenolsulphonic acids, nitroethane, phenylnitroethane, *o*- and *p*-nitrophenylnitroethanes, the three nitrophenols, the five dinitrophenols, dinitroethane, phenyldinitromethane, nitroform, and phenylcyanonitromethane. These all show the same high conductivities, varying slightly with the nature of the cation, but free from abnormalities.

J. C. W.

Electrolytic Conductivity in Non-aqueous Solutions. III. Relations between the Conductivity of the Solute and several Physical Properties of the Solvent. HENRY JERMAIN MAUDE CREIGHTON (*J. Franklin Inst.*, 1919, 187, 313—318).—The results obtained in a previous paper (this vol., ii, 44) for the electrical conductivity of *p*-tolyltrimethylammonium iodide in thirteen organic solvents are used in considering the relationship between conductivity, viscosity, and association. The formula suggested

by Jones, $\Lambda v'/\eta/x = \text{constant}$, where $\Lambda v'$ is the equivalent conductivity of comparable equivalent solutions and η and x are the coefficient of viscosity and the association factor of the solvent respectively, is found to hold approximately at 25° for acetone, propaldehyde, propionitrile, nitromethane, epichlorohydrin, benzaldehyde, formic acid, and anisaldehyde, the mean value being 0.33 and the extremes 0.242 and 0.391. Methyl and ethyl alcohols, and especially acetic acid (0.054), give lower values, and benzonitrile and nitrobenzene higher values. The expression $\Lambda_\infty \eta$, which Jones also showed to be constant, has a mean value for these solvents, except formic and acetic acids, of 0.56 at 25° . A comparison of the percentage dissociation of *p*-tolyltrimethylammonium iodide in the same solvents, at three different dilutions, with the dielectric constants (ϵ) of the solvents shows the latter to be only one factor in deciding the former; the amount of polymerisation of the solvent appears also to be an important factor. This is shown in the figures for methyl alcohol ($\epsilon = 32.5\text{--}34.8$, $x = 3.43$) and nitrobenzene ($\epsilon = 33.4\text{--}37.4$, $x = 0.93$), in which the percentage dissociations at a dilution of $v = 128$ are 79 and 66 respectively. Similar variations are found in the figures for propionitrile, benzonitrile, and epichlorohydrin.

B. V. S.

Calculation of the Chemical Constants of Polyatomic Gases. AMÉLIE LANGEN (*Zeitsch. Elektrochem.*, 1919, 25, 25—45).

—A theoretical paper in which the chemical constants of oxygen, nitrogen, nitric oxide, carbon monoxide, carbon dioxide, water, and ammonia are calculated for the normal condition, and the following values obtained: nitric oxide, +0.92; oxygen, 1.021—0.539; carbon monoxide, -0.04; nitrogen, -0.05; carbon dioxide, -0.406; water, -1.930; and ammonia, -2.454. The oxygen value was obtained from four different equilibria. The results were used to calculate the Einstein function of the specific heat β_v , and the values, hydrogen 430, ammonia 67.5, water 30, carbon dioxide 7.23, oxygen 0.736, and nitric oxide 0.543 obtained. The order of the frequencies is what is to be expected from the physical properties of the substances, and can be confirmed, as far as the order of the value is concerned, from the moment of inertia of these gases.

J. F. S.

The Critical Temperature as a Single Function of the Surface Tension. MAURICE PRUD'HOMME (*J. Chim. Phys.*, 1918, 16, 405—410).

—The surface tension, γ , is connected with the temperature by the two equations $\gamma = a - bt$ and $\gamma^3 = a' - b't$ (compare A., 1916, ii, 600), which at the critical temperature become $a - bt = 0$ and $a' - b't = 0$. It is found that, for substances which obey the Eötvös-Ramsay law, $t_c = \frac{1}{2}(t_1 + t_2)$ or $t_c = \frac{1}{2}(a/b + a'/b')$. This also holds good for liquefied gases. Amongst substances which do not obey the Eötvös-Ramsay law, the organic acids conform fairly closely to the above equation, whilst the alcohols, phenols, etc., obey the simple relationship $\gamma = a - bt$.

W. G.

Vapour Pressure Regularities. II. W. HERZ (*Zeitsch. Elektrochem.*, 1919, **25**, 45—46. Compare *ibid.*, 1918, **24**, 333).—The author has calculated the value of the constant c of the Ramsay and Young vapour pressure formula $\theta_1/\theta_2 = T_1/T_2 + c(\theta_1 - T_1)$ for chlorine, bromine, iodine, oxygen, sulphur, nitrogen, phosphorus, arsenic, bismuth, argon, krypton, xenon, copper, silver, zinc, cadmium, mercury, tin, and lead, and finds that the value is not constant in a single case. In the case of the non-metals there is an approximation to a constant, but in the case of the metals the divergence is sometimes so great that the sign changes. These constants depend in a high degree on the boiling points, and it seems likely that the inconstancy may be due to inaccuracies in the determination of the boiling points. J. F. S.

Thermodynamics and Fractional Distillation. C. MARILLER (*Bull. Assoc. Chim. Sucr. Dist.*, 1918, **35**, 45—51).—Chenard's assertion that the vapours produced on distilling mixtures of alcohol and water tend to separate into layers of different density (A., 1914, ii, 623; 1916, ii, 175) is refuted on theoretical and experimental grounds. Using apparatus similar to Chenard's, and guarding against external cooling, the author found no evidence of stratification. J. H. L.

Formula giving the Density of a Fluid in the Saturated State. E. ARIÈS (*Compt. rend.*, 1919, **168**, 714—717).—The formula deduced is $v_1 - v_2 = \Gamma(y_1 - y_2)RT_c/8P_c$, where v_1 is the volume of the molecular mass of the fluid entirely in the state of vapour, and v_2 entirely in the liquid state, these thus giving the densities in the two states of saturation. The author has tested this formula in the case of carbon dioxide, stannic chloride, methyl formate, and heptane, and finds that his calculated results agree closely with those observed by Young. W. G.

Reasons for the Movements of Camphor [on Water] and Allied Phenomena. J. GEPPERT (*Physikal. Zeitsch.*, 1919, **20**, 78—83).—A number of experiments are described showing that many substances, such as phenacetin, acetanilide, chloral hydrate, sulphonal, menthol, thymol, atropine sulphate, phthalic acid, and quinine, exhibit the same violent movements as camphor does on the surface of clean water. The rate of movement of oily substances, such as oleic acid, is also considered. The reasons for the movement are attributed to solution of the solid and also of the vapour, and the back pressure thereby occasioned. J. F. S.

Adsorption Compounds. II. R. HALLER (*Kolloid Zeitsch.*, 1919, **24**, 56—66. Compare A., 1918, ii, 259).—A continuation of previous work on adsorption compounds; 0.5 gram of the dyes *m*-nitro-*p*-toluidine-red, *m*-nitroanisidine-red, *p*-nitro-*o*-anisidine-red, Sudan-G, Sudan-I, *p*-nitroaniline-red, alizarin-yellow G.G.W., fast-orange-O, brilliant orange, chromotrope 2R

ponceau 2G, and *p*-nitrobenzeneazonaphtholsulphonic acid, dissolved in 50 c.c. of water, were treated with a 1% solution of brilliant-green as long as the latter was adsorbed. The adsorption products were isolated and characterised, and the colours produced when they were used to dye wool and cotton with tannic acid were noted.

J. F. S.

Laws of the Capillary Rise in Porous Paper. HANS SCHMIDT (*Kolloid. Zeitsch.*, 1919, **24**, 49—56).—A number of experiments are described, designed to ascertain the connexion between the rise of an acid solution in filter paper and the extent to which a drop of the liquid spreads itself when allowed to fall on to a sheet of the same paper. It is shown that the amount of spreading is the same whether the porous paper is horizontal or vertical in the case of dilute solutions of hydrochloric acid.

J. F. S.

Retardation by Sugars of Diffusion of Acids in Gels. JOHN ARTHUR WILSON (*J. Amer. Chem. Soc.*, 1919, **41**, 358—359).—A criticism of a paper by Graham and Graham (this vol., ii, 50). Compare Procter and Wilson (T., 1916, **109**, 307) and J. A. and H. W. Wilson (A., 1918, ii, 260).

J. F. S.

Osmosis and Swelling of Disperse Systems. WO. OSTWALD and K. MÜNDLER (*Kolloid. Zeitsch.*, 1919, **24**, 7—27).—A theoretical paper in which it is shown that the directly measured osmotic pressure of disperse systems is made up of two quantities: (i) the strict osmotic pressure, and (ii) an additional pressure, which is termed solvation, or swelling pressure. On the basis of this idea, a general solvation equation is established, $P_b = RTc_1 + kc_2^n$, in which P_b is the experimentally observed osmotic pressure, c_1 is the osmotic concentration, c_2 the swelling concentration, and k and n are constants. With dilute molecular or suspensoid dispersoids, the second factor of the equation disappears, and it passes over to the usual gas equation. On the other hand, in concentrated dispersoids, particularly in swelling gels, the osmotic concentration is very small, so that the first factor of the equation may be neglected. The expression $P_b = kc^n$ then, according to Posnjak and Freundlich, actually represents the dependence of the swelling pressure on the concentration in the case of gelatin and caoutchouc. The complete equation is applied to the osmotic measurements of solutions of sucrose, levulose, and lactose of Morse, and Berkeley and Hartley, over the range 0.1*N*—2.0*N* and 0—80°. The agreement between the values calculated by the formula and the experimental values is excellent. In the case of sugar solutions, $n = 2$, so that as a first approximation the equation becomes $P_b = RTc_1 + kc_2^2$, but the value varies with the nature of the sugar and with the temperature. The osmotic pressure of very concentrated solutions of calcium ferrocyanide can be represented by the above equation to within 0.6%. In the case of con-

centrated sugar and calcium ferrocyanide solutions, the share of the total pressure due to the swelling pressure is very large. It increases, for example, with sucrose, with the concentration from 5% to 63% of the total pressure, and in the case of calcium ferrocyanide to 71%. It is also shown that the osmotic pressure of the hydrosols of iron, thorium hydroxide, and copper ferrocyanide follows the reduced solvation formula and also the swelling formula of Posnjak and Freundlich, a confirmation of the view that the taking up of water by such dispersoids is to be regarded more as the swelling of a liquid colloid than a simple osmotic process. The solvation formula does not hold for those systems in which internal changes in the state of aggregation occur with changes in concentration. The value of n lies always between 1.5 and 4.0, but most often it is found between 2 and 3. J. F. S.

Theory of Solubility. ALBERT COLSON (*Compt. rend.*, 1919, 168, 681—684. Compare A., 1916, ii, 475).—A theoretical discussion of certain points arising out of his formula

$$425L = T(V + \epsilon)idC/dT,$$

expressing all the particularities of solubility, where L is the heat of saturation, ϵ is the contraction of the final system, V is the volume of the solvent which saturates the dissolved molecule, C is the concentration or weight of anhydrous salt in 100 grams of a solution saturated at T° . W. G.

Electrical Synthesis of Colloids. THE. SVEDBERG (*Kolloid. Zeitsch.*, 1919, 24, 1—7).—Three processes are described by which highly disperse metal colloids may be produced. The author prefers to call these processes electrothermal colloid syntheses. A thin sheet of gold or silver is attached by gum arabic to a plate of glass which is immersed in ethyl alcohol. Two iron wires, attached to a 440-volt circuit and arranged to carry 10 amperes, are inserted in the liquid and brought into contact with the metal foil. Immediately, the metal round the iron poles is vaporised, and on condensation in the alcohol produces alco-sols. In the second process, narrow strips of gold, silver, zinc, and tin foil are attached to glass plates in the above-mentioned manner. The ends of the strips are thickened by a somewhat thicker piece of copper. Two iron wires, as before, are brought into contact with the copper, when the strip of foil between is entirely converted into the sol. In the third method, thin wires or strips of platinum, copper, lead, zinc, and aluminium are fastened to two thick iron wires immersed in alcohol, and a current passed, when the sols of these metals are produced. The process consists in the melting of the metal, which forms a number of small globules by capillary forces, and between which a number of small arcs are set up. This vaporises the metal, which condenses in the cooler regions to form highly disperse sols. The production of the sol depends more on the current strength than on the voltage employed. J. F. S.

Colours of Colloids. II. WILDER D. BANCROFT (*J. Physical Chem.*, 1919, **23**, 1—35. Compare A., 1918, ii, 102).—A continuation of the discussion commenced in a previous paper (*loc. cit.*). The various colour effects produced by reflection and refraction of light are particularly considered in this communication.

J. F. S.

Colloid Chemistry of Indicators. II. WOLFGANG OSTWALD (*Kolloid. Zeitsch.*, 1919, **24**, 67—69. Compare A., 1912, ii, 439).—In a previous paper the author advanced the view that the colour change of indicators in many cases is a colloidal or disperse chemical process. The present paper is a résumé of the results of experiments on congo-rubin, which tend to substantiate the author's view. In aqueous solution, congo-rubin (sodium salt of benzidinebisazo- β -naphtholsulphonaphthionic acid) is a highly disperse system, intermediate between that of a typical colloid and a molecular disperse system. It is negatively charged and has a red colour, which is changed to blue by the addition of acids. This change is also brought about by the addition of a large number (seventy-five) of neutral salts, by alkaline salts, such as sodium carbonate, and by bases like barium hydroxide. On dilution, the blue solutions again become red; elevation of temperature, or the addition of alcohol, acetone, or pyridine, brings about the same reversal of colour change. By a further addition of an electrolyte to the blue solution, a precipitation of the colour substance is effected. The precipitate, on washing with water, passes into solution as a blue to violet hydrosol. It is stated that the blue solutions are less highly disperse than the red solutions, and on keeping a solution which has just turned blue, a slight precipitation occurs, which leaves a red solution. This solution may be turned blue by further addition of electrolyte. The red solutions contain a still more highly disperse orange-coloured fraction.

J. F. S.

Oscillation Method for Measuring the Size of Ultra-microscopic Particles. P. V. WELLS and R. H. GERKE (*J. Amer. Chem. Soc.*, 1919, **41**, 312—329).—The diameter of the particles of gaseous dispersoids (in smoke) has been determined by an oscillation method. A quantity of the smoke is brought into the field of an ultramicroscope which lies in a rapidly alternating electrostatic field, and the path of the particles photographed. In this way the actual oscillations are obtained, and a measurement of the amplitude gives the distance travelled by the particle between two reversals of the current. Then, by Stokes's law, the motion of a particle in an electrostatic field is given by $Xe = 3\pi\eta dv$, where X is the field in volts per cm., e the electronic charge (that is, 1.59×10^{-20}), d the diameter in cm., η the viscosity of the medium, and v the velocity. It is shown that the diameter varies from 5×10^{-6} to 10^{-4} , and that the particles rapidly coalesce.

J. F. S.

Chemical Resistance. II. Applications of the Theory of Quanta to Chemical Dynamics. SHINKICHI HORIBA (*Mem. Coll. Sci. Kyoto Imp. Univ.*, 1918, **3**, 223—234. Compare A., 1916, ii, 305).—A mathematical paper in which, by an application of the theory of quanta, and on the hypothesis: "The reacting substances can only react when they are present in a certain elemental sphere of a reaction in a stoicheiometrical relation by their own kinetic energy, but the reaction will begin only when they are transformed into an active form by absorbing some energy from the surrounding medium," calculations of chemical resistance have been carried out. On this hypothesis of the mechanism of a chemical reaction, chemical resistance can easily be separated into two terms: (1) a term inversely proportional to the probability that the molecules of the reacting substances encounter in a stoicheiometrical relation in an elemental sphere by their own kinetic energy, and (2) a term proportional to the probability of the energy transport to reacting molecules from their surrounding medium.

J. F. S.

Crystal Gratings and Bohr's Atom Model. M. BORN and A. LANDE (*Ber. deut. physikal. Ges.*, 1918, **20**, 202—209).—A mathematical paper in which the radius and number of electrons situated in the various rings of the metals of the alkalis and of the halogens are calculated. The elastic compressibility of the alkali haloids is calculated, and values obtained are about twice as large as the experimentally determined values. The absolute dimensions of the grating constant, δ , have been calculated, and the values indicate that the substances are twice as soft as the theory demands.

J. F. S.

Calculation of the Compressibility of Regular Crystals from the Theory of the Grating. M. BORN and A. LANDE (*Ber. deut. physikal. Ges.*, 1918, **20**, 210—216. Compare preceding abstract).—The compressibility of the chloride, bromide, and iodide of sodium, potassium, and thallium has been calculated by means of the formula $x = 4.26 \times 10^{-14}([\mu_+ + \mu_-]/\rho^2)$ on the basis that $n=9$ and not 5, as was taken to be the case in the previous paper. The value of n has been calculated from the observed compressibilities, and a mean value 8.76 obtained. Using the value 9, a good agreement is found between the calculated and experimental values. In the case of calcium fluoride, to which the calculations were extended, $x = 1.10 \times 10^{-12}$, whilst the experimental value is 1.16×10^{-12} .

J. F. S.

The Cubic Atom Model. M. BORN (*Ber. deut. physikal. Ges.*, 1918, **20**, 230—239).—The author, from a survey of the properties of the halogen derivatives of the alkalis, considers the cubic atom model is well founded, and whilst holding to the principles set down by Bohr, considers the matter mathematically with the object of bringing certain abnormalities into line with the general

theory. The question of the tetrahedral carbon atom is also considered. J. F. S.

Calculations of Ionic Charges in Crystals. J. WIMMER (*Physikal. Zeitsch.*, 1919, **20**, 92—93).—A theoretical paper in which it is shown that the ionic charges of diatomic crystals or crystals which can be regarded as made up of two equivalent atomic groups, and for which the grating structure is known, can be calculated by means of the formula $v/z = (G_1 + G_2) / \sqrt{G_1 G_2}$, in which v represents the valency, z the number of electrons, and G_1 and G_2 the atomic or molecular weights of the atoms or groups composing the molecule. The charges have been calculated for the crystals potassium chloride, sodium chloride, calcium fluoride, silica, calcium carbonate, potassium bromide, potassium iodide, sodium fluoride, lithium fluoride, and zinc sulphide. In the case of the first-named five substances, the value of the Drude constant k has been calculated. J. F. S.

The Theory of Duplex Affinity. SAMUEL HENRY CLIFFORD BRIGGS (*T.*, 1919, **115**, 278—291).

Laboratory Apparatus for Rapid Evaporation. E. C. MERRILL and CLARE OLIN EWING (*J. Ind. Eng. Chem.*, 1919, **11**, 230).—Rapid evaporation of liquids is effected by passing a blast of heated air across the basin on the steam-bath. The air is forced through a brass cylinder containing cotton wool to act as a filter, and then through a copper coil, which is heated in the bath, and the outlet of which is connected with a series of blowers. Each of these is provided with a glass tap, and its height above the basin can be adjusted as desired. [See, further, *J. Soc. Chem. Ind.*, 1919, 268A.] C. A. M.

Theobald van Hogelande. F. M. JAEGER (*Chem. Weekblad*, 1919, **16**, 179—180).—The work "Merces Alchimistarum," Frankfurt-am-Mayn, 1610, attributed to Theobald van Hogelande (A., 1918, ii, 437), is shown to be a reprint of a German translation of his "De Alchimiae Difficultatibus," Frankfurt, 1600.

W. S. M.

Inorganic Chemistry.

An Unusual Sulphur Crystal. F. RUSSELL BICHOWSKY (*J. Washington Acad. Sci.*, 1919, **9**, 126—131).—A crystallographic description is given of a well-developed crystal, D 2·01, of sulphur which was obtained accidentally by adding a hot alcoholic solution of ammonium polysulphide to a mixture of benzonitrile, hydroxylamine hydrochloride, and ether.

L. J. S.

The Behaviour of Sulphur towards Carbonaceous Matter at High Temperatures. J. P. WIBAUT (*Rec. trav. chim.*, 1919, **38**, 159—162).—When sugar, or the carbon obtained by charring it, or wood charcoal, is mixed with sulphur and the mixture heated in a closed crucible to a bright red incandescence, in each case a product is obtained which, after extraction first with carbon disulphide and then with ether, is found to contain sulphur to the extent of from 3—6%. Whether this sulphur is chemically combined or only absorbed is not decided. W. G.

Tellurium Sulphide. AARON M. HAGEMAN (*J. Amer. Chem. Soc.*, 1919, **41**, 329—341).—The introduction of hydrogen sulphide into an aqueous solution of tellurous acid at ordinary temperatures or below causes the immediate production of a reddish-brown precipitate, which is represented by the formula TeS_2 . The production of this compound is independent of the acid concentration. At temperatures below -20° , tellurium sulphide is a stable compound, but at temperatures above -20° , dissociation takes place. At temperatures near -20° this dissociation is slow, whilst at higher temperatures dissociation takes place more rapidly. The degree of dissociation at any time or temperature may be determined by the amount of sulphur which can be extracted by carbon disulphide. Dissociation never continues to completion. The dissociated mass extracted with carbon disulphide always retains at least 0.95% sulphur. This sulphur does not exist as a sulphide of tellurium which is decomposed by hydrochloric or hydrobromic acid of any strength, nor does it exist as a variety of sulphur insoluble in carbon disulphide. The compound $\bullet\text{TeS}$, often described, has no existence. The production of TeS_2 is independent of the medium in which the reaction is effected, for the action of hydrogen sulphide on solutions of tellurium tetrachloride in a large number of organic solvents gave exactly the same product. The dissociation and stability of tellurium sulphide is solely a question of temperature. Tellurium tetrachloride is found to be soluble in benzene, toluene, methyl alcohol, ethyl alcohol, *n*-butyl alcohol, amyl alcohol, benzyl alcohol, xylene, chloroform, and ethyl acetate, sparingly so in light petroleum, benzaldehyde, acetone, isopropyl bromide, and carbon tetrachloride, and insoluble in carbon disulphide. J. F. S.

Formation of Ammonia at High Temperatures. E. BRINER (*Helv. Chim. Acta*, 1919, **2**, 162—166. Compare this vol., ii, 148).—A discussion of Maxted's recent work (T., 1918, **113**, 168, 386). In the first place, it is shown that the T^2 terms in Maxted's two formulæ have merely a corrective influence, and consequently they cannot be very significant in regions of temperature in which they have not been tested experimentally. This explains the great divergences between the values of K obtained from the two formulæ; at 1000° abs., up to which point both formulæ have been tested by experiment, there is agreement; at 2000° , the first

formula gives a value for K which is three times that derived from the second; at 3000° , the ratio is 10 to 1, and at 4000° , 100 to 1. Furthermore, assuming that at high temperatures the reaction is of the same nature as at lower temperatures, namely, one between molecules of nitrogen and hydrogen, these gases should unite completely at about 6000° , according to the first formula, and, in general, a gaseous mixture should become more and more complex with rise of temperature. This is contrary to the conclusions obtained by spectroscopic investigations, which clearly prove the elementary nature of the substances present in the hottest stars.

Such difficulties disappear if account is taken of the dissociation of the molecules into atoms (compare A., 1916, ii, 215). According to recent investigations, gases like hydrogen contain appreciable proportions of free atoms at much lower temperatures than was at one time supposed. The extra production of ammonia at high temperatures may be explained, therefore, by the greater kinetic energy of the free atoms of nitrogen and hydrogen. J. C. W.

Potassium Ammonosodiate, Potassium Ammonolithiate, Rubidium Ammonosodiate, and Ammonolithiate. EDWARD C. FRANKLIN (*J. Physical Chem.*, 1919, **23**, 36—53).—A number

of reactions between metallic amides in ammonia solution have been carried out, and as a result several ammono-salts have been isolated and characterised. These salts stand in the same relationship to ammonia as do the zincates, aluminates, and plumbites to water. A very complete list of the ammono-salts hitherto prepared is given. *Dipotassium ammonosodiate*, $\text{NaNK}_2 \cdot 2\text{NH}_3$ or $\text{NaNH}_2 \cdot 2\text{KNH}_2$ or $(\text{Na}[\text{NH}_2]_3)\text{K}_2$, is prepared (i) by the action of potassamide on sodamide in liquid ammonia solution, (ii) by the action of sodium iodide on an excess of potassamide in liquid ammonia, and (iii) by the action of sodium on potassamide in liquid ammonia in the presence of a small quantity of platinum black. This compound crystallises well, and does not lose ammonia at 100° in a vacuum; at higher temperatures it melts, loses ammonia, and attacks the containing glass vessel. *Mono-rubidium ammonosodiate*, $\text{NaNHRb} \cdot \text{NH}_3$ or $\text{NaNH}_2 \cdot \text{RbNH}_2$ or $(\text{Na}[\text{NH}_2]_2)\text{Rb}$, is formed by the action of sodium and rubidium simultaneously on liquid ammonia. This compound is readily soluble in liquid ammonia, and is violently decomposed by water with the formation of the hydroxides of the metals. *Dirubidium ammonosodiate*, $\text{NaNRb}_2 \cdot 2\text{NH}_3$ or $\text{NaNH}_2 \cdot 2\text{RbNH}_2$ or $(\text{Na}[\text{NH}_2]_3)\text{Rb}_2$,

is formed from the mother liquors of the previous compound by the addition of a large excess of rubidamide. This compound is considerably more soluble than the preceding compound in liquid ammonia. *Dipotassium ammonolithiate*, $\text{LiNK}_2 \cdot 2\text{NH}_3$ or $\text{LiNH}_2 \cdot 2\text{KNH}_2$ or $(\text{Li}[\text{NH}_2]_3)\text{K}_2$, is prepared by the action of potassamide on lithium iodide in liquid ammonia solution, and also by the action of lithium and potassium simultaneously on liquid

ammonia in the presence of platinum black. The salt forms minute, colourless crystals, which are practically insoluble in liquid ammonia. It is decomposed by acid amides and ammonium salts of oxygen and halogen acids (that is, by ammono-acids), with the formation of the corresponding salts of lithium, potassium, and ammonium. *Monorubidium ammonolithiate*, LiNHRb.NH_3 or $\text{LiNH}_2.\text{RbNH}_2$ or $(\text{Li}[\text{NH}_2]_2)\text{Rb}$, is prepared by the action of an excess of a solution of rubidamide in ammonia on metallic lithium in the presence of platinum black. A white, crystalline compound is obtained, which is sparingly soluble in liquid ammonia. It is decomposed by ammono-acids and by water, as in the preceding case. Attempts were made to separate rubidamide from potassium-amide by crystallisation from liquid ammonia, but without success, for these two substances form isomorphous mixtures which are relatively richer in rubidamide than the solution from which they separate.

J. F. S.

Thermal Decomposition of certain Inorganic Trinitrides.

E. MOLES (*J. Chim. Phys.*, 1918, **16**, 401—404. Compare *ibid.*, 1917, **15**, 51).—A claim for priority over Hitch (compare A., 1918, ii, 398).

W. G.

Method of Treating Beryl for the Extraction of Glucinum.

H. COPAUX (*Compt. rend.*, 1919, **168**, 610—612).—One part of powdered beryl is heated with two parts of sodium silicofluoride at 850° for thirty to forty minutes. At this temperature, the sodium silicofluoride decomposes, giving silicon fluoride, which attacks the beryl, giving glucinum fluoride and aluminium fluoride, which in turn combine with the sodium fluoride to give the corresponding double fluorides. The material is extracted with boiling water, in which the sodium glucinum fluoride dissolves, and the extract, after filtration, contains practically the whole of the glucinum in this form along with a little alumina and silica. A slight excess of boiling sodium hydroxide solution is added to the filtrate, and the precipitated oxides are collected and redissolved in sulphuric acid. The solution is concentrated, and the glucinum sulphate is allowed to crystallise out. By this method, 90% of the glucinum present in the mineral may be readily recovered.

On this process is based a method for the estimation of glucinum in beryl, using four parts of sodium silicofluoride to one part of beryl. The precipitation with sodium hydroxide is omitted, and an aliquot portion of the filtered aqueous extract is evaporated with an excess of sulphuric acid in a platinum dish until white fumes appear. The residue is dissolved in water, and an excess of ammonium hydroxide is added. The precipitate is filtered off, washed, dried, ignited, and weighed. Any silica in it is removed by means of hydrofluoric acid, and the aluminium and glucinum oxides are separated by Wunder and Weger's method (compare A., 1912, ii, 687).

W. G.

Reaction between Sodium Chloride Solution and Metallic Magnesium. WILLIAM HUGHES (T., 1919, 115, 272—277).

The Hammer-hardening of Lead, Tin and Thallium. PAUL NICOLARDOT (*Compt. rend.*, 1919, 168, 558—560).—Lead, thallium, and tin all undergo hammer-hardening, but they anneal spontaneously at the ordinary temperature, the rate of annealing rising with rise in temperature. W. G.

The Extraction of Thallium from Pyrites Flue Dust. GEORGE SISSON and J. S. EDMONDSON (*J. Soc. Chem. Ind.*, 1919, 38, 70T).—The dust collected from the flues situated between the pyrites kilns and the Glover tower of a sulphuric acid plant was found to contain 0.25% of thallium, representing about one part of thallium per million of pyrites burnt. The thallium was isolated by extracting the dust with dilute sulphuric acid and precipitating with hydrochloric acid. The crude thallium chloride was purified, dried, and reduced to metal by fusion with potassium cyanide and sodium carbonate, or, alternatively, with zinc. E. H. R.

Chemistry of Aluminium and Aluminium Alloys. JOHN G. A. RHODIN (*Trans. Faraday Soc.*, 1919, 14, 134—149).—Experiments dealing with the working up of scrap aluminium are described. The specific gravity of aluminium containing various quantities of an equal mixture of copper and zinc has been determined, and it is shown that the density curve rises rapidly, but with decreasing rate, to 90% aluminium; between 90% and 80% aluminium, the curve is a slowly rising straight line which has an inflexion point somewhere about 76%. Aluminium is stated to dissolve alumina, and a method is devised for the estimation of the metallic aluminium apart from the alumina. A quantity of an aluminium alloy (2 grams) is placed in a tall beaker with 60 c.c. of 10% sodium hydroxide solution and heated on a sand-bath until the reaction becomes violent, after an induction period, when it is removed and cooled. The reaction is then completed by further heating on the sand-bath. The black residue is collected and dissolved in nitric acid (D 1.2). The two solutions thus obtained are analysed according to well-known methods. Comparison of the analytical results with the composition deduced from the specific gravity of the alloy showed a remarkably good agreement. By heating pure aluminium powder in air until the increase in weight corresponds with the formation of a compound Al_2O_3 , a light grey, non-metallic powder is obtained. Boiling this powder with 10% sodium hydroxide dissolves a portion of it and leaves insoluble a light grey oxide, Al_3O_4 . A number of determinations of the specific heat of aluminium alloys of copper and zinc are given. The following values were obtained: 98.6% aluminium, 0.2081; 90% aluminium, 10% copper, and 10% zinc, 0.1918; 80% aluminium, 20% zinc, 0.1844.

In the discussion on the paper, CLAUDE T. J. VAUTIN stated

that he had isolated the oxide Al_2O_3 , a compound which produced a brilliant light under air oxidation.

J. F. S.

The Formation of Troostite at Low Temperature in Carbon Steels and the Influence of the Temperature of Emersion in Interrupted Tempering. A. PORTEVIN and GARVIN (*Compt. rend.*, 1919, 168, 731—733).—With velocities of tempering considerably higher than the critical velocities, by interrupting the tempering, very marked reheating may be observed, at temperatures down to 450° , and troostite is formed. The troostite is formed directly and immediately from the solid solution γ -iron-carbon at temperatures much lower than those at which it is formed by continuous tempering. With a velocity of tempering near to that of the critical velocity, it was possible to observe the formation of troostite at even lower temperatures (380°). If the velocity is inferior to the critical velocity, the reheating being produced at high temperatures during the period of rapid cooling, troostite is always obtained, and the temperature of emersion does not appreciably affect the structure and the hardness. With rapid tempering, it is possible, without appreciably altering the hardness, to stop the tempering at temperatures in the neighbourhood of 350° .

W. G.

Structure of Iron-Carbon-Chromium Alloys. TAKEJIRO MURAKAMI (*Sci. Rep. Tohoku Imp. Univ.*, 1918, 7, 217—276).—An investigation of the structure of 115 chromium-iron, chromium-carbon, and iron-carbon-chromium alloys. The influence of chromium on the magnetic critical point from A_2 was investigated, and it was found that it decreases at first slowly and then rapidly as the chromium content increases.

In the annealed alloys, the chromium carbide present is Cr_4C . At high temperatures, this decomposes into Cr_3C_2 and chromium. Three double carbides of iron and chromium were detected, namely, $\text{Fe}_3\text{C}, \text{Cr}_4\text{C}$, $(\text{Fe}_3\text{C})_9, \text{Cr}_4\text{C}$, and $(\text{Fe}_3\text{C})_{18}, \text{Cr}_4\text{C}$. A portion of a thermal equilibrium diagram for the ternary system was drawn up. The binary system iron-chromium is a continuous series of solid solutions with a minimum about 70% of chromium. In the solid state, a certain undetermined solubility of the carbide Cr_4C in chromium occurs. Cr_4C and the double carbide $(\text{Fe}_3\text{C})_9, \text{Cr}_4\text{C}$ form an uninterrupted series of solid solutions. The eutectic in the Cr_4C -Cr series occurs at about 1.8%. [See, further, *J. Soc. Chem. Ind.*, 1919, 257A.]

F. C. TH.

The Reduction of Tungstic Oxide. C. W. DAVIS (*J. Ind. Eng. Chem.*, 1919, 11, 201—204).—To obtain a satisfactory reduction of tungstic oxide to metallic tungsten, the material must be freed from water, which is best effected by a current of air at about 500° . On reducing the dried oxide with carbon, a blue or purple oxide is produced at 650° to 850° , a chocolate-brown mixture of oxides at 900° to 1050° , and metallic tungsten above 1050° .

The proportion of carbon required for the reduction ranges from 1:10 to 1'6:10, according to the temperature, time, and other conditions. Excess of carbon can be removed to a considerable extent by washing the product with water. When hydrogen is used as the reducing agent, the mixture of brown oxides is formed at 800° to 900°, whilst at 1080° a pure tungsten deposit (for example, 99·4%) is obtained. Reduction with gasoline vapour yields a product containing about 98% of tungsten with a considerable amount of carbon. [See, further, *J. Soc. Chem. Ind.*, 1919, 260A.] C. A. M.

The Partial Purification of Zirconium Oxide. A. J. PHILLIPS (*J. Amer. Ceram. Soc.*, 1918, **1**, 791—800).—Zirconia may be freed from iron oxide by mixing it with 4% of finely ground petroleum coke, making the mixture into balls, and heating them at 900° in a vertical cylindrical furnace (heated externally) through which a current of moist chlorine is passed. The reversible reaction $\text{FeCl}_3 = \text{FeCl}_2 + \text{Cl}$ constantly tends to form an equilibrium, which leaves some of the iron in the zirconia. If the rate of passage of the chlorine is increased beyond the requisite chlorine tension, chlorine is absorbed until the tension is reduced. With insufficient chlorine, the ferrous chloride is reduced. The water vapour present serves to produce hydrogen chloride, in which the ferrous chloride is readily volatile, whilst the zirconia is not affected. Hydrogen chloride without any free chlorine does not reduce the iron oxide below 0·5%. If the zirconia is heated by passing hot gases through it, the action of the chlorine is irregular and inefficient. Various methods of purification by fusing the zirconia with various salts proved unsatisfactory as far as the removal of the iron was concerned. [See *J. Soc. Chem. Ind.*, 1919, 252A.] A. B. S.

Mineralogical Chemistry.

Pyromorphite Group. M. AMADORI (*Gazzetta*, 1919, **49**, i, 38—102).—A summary and discussion of previous papers (A., 1913, ii, 216; 1915, ii, 358; 1918, ii, 365). T. H. P.

Non-identity of the Copper Silicates, Plancheite and Shattuckite. WALDEMAR T. SCHALLER (*J. Washington Acad. Sci.*, 1919, **9**, 131—134).—A reply to F. Zambonini (A., 1918, ii, 170). Although his new analysis of plancheite from the French Congo leads to nearly the same formula, $6\text{CuO}, 5\text{SiO}_2, 2\text{H}_2\text{O}$, as that for shattuckite ($2\text{CuO}, 2\text{SiO}_2, \text{H}_2\text{O}$) from Arizona, the difference in the refractive indices is sufficient to prove that the two minerals are distinct. The highest value for plancheite ($\alpha=1.645$, $\gamma=1.715$) is less than the lowest value for shattuckite ($\alpha=1.752$, $\gamma=1.815$). L. J. S.

Analytical Chemistry.

A New Indicator for Bases and Acids. MARC CHAUVIERRE (*Bull. Soc. chim.*, 1919, [iv], **25**, 118—119).—The reagent is prepared by boiling red beetroot with water and filtering the extract. It is a violet-red, opalescent solution, which is turned deep yellow with alkalis and retains its colour with acids. It is sensitive to both weak and strong inorganic and organic acids. Its colour is restored by sulphuric acid diluted to 1 in 10,000. Test papers cannot be prepared from it, as it does not fix on paper. W. G.

End-point in Oxidation Titrations determined by means of the Potentiometer. I. M. KOLTHOFF (*Chem. Weekblad*, 1919, **16**, 408—416).—When a reducing agent is titrated by means of an oxidising agent, the potential difference between the solution and an irreversible electrode immersed in it, measured against a normal electrode, varies in value during the titration, and in the neighbourhood of the end-point undergoes a rapid change. Expressions are deduced for the *E.M.F.* at the end-point and for the equilibrium constant of the reaction in terms of the normal potentials of the oxidising and the reducing agents. With the help of these, the sharpness of the end-point is discussed in relation to the magnitude of the equilibrium constant. W. S. M.

Arsenious Oxide as a Standard Substance in Iodometry. ROBERT M. CHAPIN (*J. Amer. Chem. Soc.*, 1919, **41**, 351—358).—Using weight burettes, solutions of highly purified arsenious oxide have been tested as to their trustworthiness as standards in place of iodine solutions. In six titrations of pure arsenious oxide against pure iodine, very precise results were obtained, the average of which agreed to within 1 in 3600 of the theoretical value. It is shown that arsenious oxide is a more trustworthy standard than iodine for volumetric work. Arsenious oxide is non-hygroscopic, and is permanent in both the solid state and in solution. The precautions necessary in the use of both arsenious oxide and iodine are discussed. J. F. S.

An Automatic Burette. GEORGE J. HOUGH (*J. Ind. Eng. Chem.*, 1919, **11**, 229).—The base of the burette consists of a glass tube with an outer jacket, which is passed through an opening in a rubber stopper made to fit into the mouth of the solution bottle. At the side of the jacket is a tube, to which can be attached a rubber pressure bulb, and it also has a side-tube intended to be closed with the finger when air is blown into the bottle. To equalise the pressure, a small hole is provided in the jacket above the level of the liquid in the bottle. When filled, the burette is

closed by a tap at the base, and the solution is drawn off through a side-tubulure ending in a tap. C. A. M.

Chlorine Absorption and Chlorination of Water. ABEL WOLMAN and LINN H. ENSLOW (*J. Ind. Eng. Chem.*, 1919, **11**, 209—213).—A series of experiments on different waters to determine the velocity of absorption of available chlorine by the same water during varying intervals of time has shown that the velocity constant, K ($K = 1/t_2 - t_1 \cdot \log N_1/N_2$), decreases, as a rule, with the time of contact. In the case of water containing little organic matter, however, it tends to become constant for different time intervals. The use of colour readings as an index of chlorine absorption is only trustworthy under known conditions with a given water, and the same conclusion applies to the measurement of the turbidity. The chlorine absorption does not increase in direct proportion with the increase in pollution (as measured by oxygen absorption), but shows a decreasing acceleration. The experiments cited appear to indicate that a thirty-minute absorption plus a high factor of safety is unnecessary, and that the addition of a small constant factor to the result, obtained by five minutes' absorption, would be as effective for the routine control of chlorination as the use of a longer time interval. [See also *J. Soc. Chem. Ind.*, 1919, 267A.] C. A. M.

Estimation of Halogens in Organic Compounds. D. VORLÄNDER (*Ber.*, 1919, **52**, 308).—The Carius method is unnecessary, except, perhaps, for very volatile substances. The author uses a modification of Baubigny and Chavanne's process (A., 1903, ii, 510; 1904, ii, 203). In the absence of iodine, the substance (about 0.4 gram) is digested with a mixture of mercurous or mercuric nitrate (1 gram), potassium dichromate (6—8 grams), and pure sulphuric acid (40 c.c.) at 130—140°, and the halogen evolved is trapped by a sulphite solution and estimated by Volhard's method. If iodine is present, silver nitrate must be used, when iodic acid is formed.

[For sketch of original apparatus, see *J. Soc. Chem. Ind.*, 1904, 136.] J. C. W.

Apparatus for the Automatic Estimation of Small Amounts of Oxygen in Combustible Gas Mixtures or of Combustible Gases in Air. H. C. GREENWOOD and A. T. S. ZEALLEY (*J. Soc. Chem. Ind.*, 1919, **38**, 87—90T).—The apparatus is designed for the purpose of detecting 0.1% or more of oxygen in gas mixtures, and of giving a continuous indication, not necessarily recorded, which will show at any moment the actual concentration. The principle involved is that of the combustion of the oxygen or other impurity by means of an intermittently heated platinum wire; automatic arrangements are provided for making and breaking the required electrical contacts, sealing up the combustion vessel during the heating period, cooling the gas, and

measuring the resulting contraction, ringing an electric bell at a specified oxygen concentration, and flushing out the spent gas by a new charge. A diagram is given of the apparatus, and the original paper should be consulted for details regarding its operation.

W. P. S.

Reagent for, and Method of Estimating, Ozone. LOUIS BENOIST (*Compt. rend.*, 1919, **168**, 612—615).—Fluorescein is a very sensitive reagent for the detection of ozone. At a dilution of 1 in 1,000,000, its solution loses its fluorescence in the presence of a trace of ozone, and is decolorised. At a dilution of 1 in 1000, it loses its fluorescence, but the solution remains yellow in colour. This phenomenon is not produced by oxygen, and it requires an enormous excess of nitrous vapours to destroy the fluorescence. Similarly, chlorine, even if present to the extent of three times the weight of fluorescein, and carbon dioxide, if present to the extent of twenty times the weight of fluorescein, do not destroy the fluorescence of a solution of fluorescein diluted to 1 in 1,000,000. Quantitative measurements indicate that the reaction takes place between two molecules of ozone and one molecule of fluorescein. An optical arrangement is described which permits of the detection of fluorescence in a solution diluted to 1 in 1,000,000,000, and thus, using 3 c.c. of such a solution, it is possible to detect and estimate 10^{-9} grams of ozone, which is a much smaller amount than can be detected by starch iodide.

W. G.

Estimation of Sulphites and of Sulphur Dioxide in Gaseous Mixtures. PERCY HALLER (*J. Soc. Chem. Ind.*, 1919, **38**, 52—56r).—A trustworthy method for the estimation of sulphites consists in titration with potassium iodate solution strongly acidified with hydrochloric acid. The addition of glycerol (about 5% of the volume of the solution) to sulphite solutions or to sodium hydroxide solution used for absorbing sulphur dioxide prevents any loss due to oxidation of the sulphite by dissolved air, even when the solution is heated. The presence of the glycerol does not interfere with the subsequent titration of the sulphite; the results obtained for sulphur dioxide in gases are much higher than are found when the sulphur dioxide is absorbed in sodium hydroxide solution to which glycerol has not been added.

W. P. S.

Estimation of Sulphates in the Presence of Iron. HERMANN KOELSCH (*Chem. Zeit.*, 1919, **43**, 117).—Examination of barium sulphate precipitates obtained in the estimation of sulphates in zinc blends (compare A., 1916, ii, 194) showed that previous removal of iron had little effect on the purity of the barium sulphate as compared with precipitates obtained after the iron had been separated. The principal impurity in the barium sulphate precipitates, in both cases, was barium chloride; it amounted to about 7% of the weight of the precipitate. It is

pointed out that an error may be introduced owing to the reduction of a portion of the sulphate to sulphide during ignition unless care is taken to ensure oxidation. [See, further, *J. Soc. Chem. Ind.*, 1919, May.] W. P. S.

Estimation of Nitrates in Soil by the Phenoldisulphonic Acid Method. H. A. NOYES (*J. Ind. Eng. Chem.*, 1919, 11, 213—218).—Extraction of the soil with cold water under specified conditions removes the whole of the nitrates present, and they may be accurately estimated by the phenoldisulphonic acid method in an aliquot portion of the filtrate. The presence of chlorides does not interfere with the estimation provided that the temperature is kept below that which causes the chlorides and nitrates to react with the dilute sulphuric acid. Organic substances which yield a coloured extract, or iron in the soil, may be removed by adding calcium hydroxide to the soil before the extraction with water. [See, further, *J. Soc. Chem. Ind.*, 1919, 265A.]

C. A. M.

Estimation of Nitro-groups in Organic Compounds by means of Stannous Chloride. J. G. F. DRUCE (*Chem. News*, 1919, 118, 133).—A modification of Young and Swain's method (A., 1898, ii, 186) for estimating nitro-groups by reduction with stannous chloride and titration of the excess of the latter with iodine solution is found to give satisfactory results (compare also Altmann, A., 1901, ii, 475). [See *J. Soc. Chem. Ind.*, 1919, 247A.]

T. H. P.

Solvent Action of Dilute Citric and Nitric Acids on Rock Phosphate. J. A. STENIUS (*J. Ind. Eng. Chem.*, 1919, 11, 224—227).—The amount of phosphorus extracted from rock phosphate by citric acid of 0.2% strength was approximately the same as that extracted by neutral ammonium citrate solution. Variations in the strength of acid and in the amounts of rock phosphate treated had a great influence on the results. Calcium carbonate and other basic substances reduce the solvent action of citric acid, and the addition of the extra quantity of acid equivalent to the basic substance does not eliminate this influence. Extraction with dilute nitric acid (0.06 to 0.015%) removes still greater amounts of phosphorus, and this acid is therefore still less suitable than citric acid for estimating the available phosphorus. Although ammonium citrate solution does not extract all the available phosphorus, yet if used under uniform conditions it affords a test of the effect of any special treatment of rock phosphate. [See, further, *J. Soc. Chem. Ind.*, 1919, 265A.]

C. A. M.

Methods of Glass Analysis, with Special Reference to Boric Acid and the Two Oxides of Arsenic. E. T. ALLEN and E. G. ZIES (*J. Amer. Ceram. Soc.*, 1918, 1, 739—786).—Tervalent and quinquevalent compounds of arsenic in glass may be separated

by heating the glass with hydrofluoric and sulphuric acids, which expel the trivalent arsenic, but leave the whole of the quinquevalent arsenic in the residue.

The quinquevalent arsenic may be estimated by precipitation as a sulphide, which is then oxidised to arsenic acid, reduced by hydriodic acid, and titrated with standard iodine solution, using starch as indicator. The total arsenic is estimated by fusing the glass with sodium carbonate and a little potassium nitrate, and determining the arsenic as just described. The nitre oxidises any arsenious compounds present, and so prevents their volatilisation. Boric acid is preferably estimated by Chapin's method, in which methyl alcohol and anhydrous calcium chloride are added to an acid solution of the fused glass, the methyl borate is distilled, and collected in sodium hydroxide solution. The methyl alcohol is removed from this by evaporation, the solution rendered acid with hydrochloric acid, heated to expel all carbon dioxide, then rendered neutral to *p*-nitrophenol by the addition of sodium hydroxide; mannitol is then added, and the free boric acid is titrated with standard sodium hydroxide. The results are affected by arsenious acid, but this can be avoided by oxidising the latter with hydrogen peroxide, as arsenic acid is inert. Relatively large amounts of fluorides affect the accuracy of the results, but the proportions usually present do not interfere. Special precautions required in the estimation of iron, zinc, lead, barium, and calcium by customary methods are described, and the suggestion is made that when analysing borosilicate glasses, the boric acid should be expelled by treating the residue obtained by evaporation (to separate the silica) with methyl alcohol before proceeding with the customary method of analysis. Attention is directed to the universal presence of hygroscopic moisture in finely powdered glass, and the effect of this on the analytical results. [For details, see *J. Soc. Chem. Ind.*, 1919, 254A.] A. B. S.

Instrument for the Estimation of Small Quantities of Carbon Monoxide in Hydrogen. E. K. RIDEAL and HUGH S. TAYLOR (*Analyst*, 1919, **44**, 89—94).—The method described depends on the preferential catalytic combustion of the carbon monoxide, the carbon dioxide formed being absorbed and estimated by measuring the conductivity of the solution. The gas (hydrogen) under examination enters the apparatus, and is measured by a gauge; it is then mixed with a small quantity of oxygen, obtained by the electrolysis of sodium hydroxide solution between nickel electrodes, and passes to a catalyst chamber. The latter contains a mixture of iron and chromium oxides, and also a small quantity of ceria and thoria, and is heated at 230°; the gases leaving the combustion chamber are passed through an absorption column, through which a current of *N*/200-calcium hydroxide solution flows at regulated speed, and the solution is collected in an electrolytic cell, where the conductivity is measured. [See, further, *J. Soc. Chem. Ind.*, 1919, 252A.] W. P. S.

[**Estimation of Glucinum in Beryl.**] H. COPAUX (*Compt. rend.* 1919, **168**, 610—612).—See this vol., ii, 192.

The Products of the Reaction of Different Metals with Quinosol. N. SCHOORL (*Pharm. Weekblad*, 1919, **56**, 325—328).—Quinosol (the potassium salt of 8-hydroxyquinoline-5-sulphonic acid) gives an extremely delicate reaction with copper salts (Saul and Crawford, A., 1918, ii, 408). The author extends the use of this reagent, or of "superol (8-hydroxyquinoline sulphate), to the detection of arsenic (arsenate), barium, mercury (mercurous), lead, strontium, tin (stannous and stannic), iron (ferrous), and silver. The reagent superol is applied in the form of a 0.2% solution in water. The precipitates produced, except in the case of iron, are microcrystalline and of extremely characteristic appearance. 0.5 Mg. of copper per litre may be detected in this way.

W. S. M.

Estimation of Lead in Lead Salts. R. L. MORRIS (*Chem. and Drug.*, 1919, **91**, 52—54).—The method described in the British Pharmacopœia for the estimation of lead in lead salts (precipitation as oxalate and titration of the precipitate with permanganate solution) yields low results unless the precipitation is made in a solution containing at least 60% of acetic acid. [See, further, *J. Soc. Chem. Ind.*, 1919, 251A.]

W. P. S.

Errors in the Analysis of Chrome Ironstone [Chromite], and a New Process. JAMES MOIR (*J. S. African Assoc. Anal. Chem.*, 1919, **2**, [i], 9—16).—From an investigation made with synthetic mixtures, it is concluded that errors amounting to 10% of the chromium present are quite possible in the analysis of chromite by the usual methods. A modification of the sodium peroxide fusion method is described by which results averaging 99.6% of the truth, with a total variation of about 1%, were obtained. [See, further, *J. Soc. Chem. Ind.*, 1919, 260A.]

W. E. F. P.

***o*-Tolidine as a Colorimetric Test for Gold.** W. B. POLLARD (*Analyst*, 1919, **44**, 94—95).—A 0.1% *o*-tolidine solution in 10% hydrochloric acid gives a bright yellow coloration with a gold chloride solution containing one part of gold in one million parts of water; the colour can just be detected in a solution containing one part in twenty millions if observed in a depth of 10 cm. of liquid. If free chlorine is present, the coloration requires about three minutes for full development. Ruthenium, iron, osmic acid, and vanadates also give a yellow coloration with the reagent, but other metals do not interfere with the test. In the presence of copper, a green coloration may be obtained instead of a pure yellow. Nitrites and other reducing substances must not be present. [See, further, *J. Soc. Chem. Ind.*, 1919, 269A.]

W. P. S.

The "Dracorubin" and "Dracorubin Capillary" Tests for Identifying and Differentiating Colourless Liquids.

KARL DIETERICH (*Ber. Deut. pharm. Ges.*, 1918, **28**, 449—492).—The test papers employed are prepared by immersing strips of filter paper, 7 cm. long by 1 cm. wide, in an alcoholic or benzene solution of the portion of Sumatra palm resin (palm dragon's blood), which is insoluble in boiling light and heavy petroleum; the strips are dried before use. When these papers are immersed in various organic liquids, the red colouring matter is removed more or less completely, according to the solvent properties of the liquid. The rate of solution, the coloration of the liquid after fifteen minutes and twenty-four hours, respectively, and the appearance of the paper after removal from the liquid, are different in the case of such liquids as alcohol, ether, petroleum, benzene, acetone, turpentine, etc. In the "capillary" test, the paper is suspended so that its lower end dips to a depth of 1 cm. in the liquid. [See, further, *J. Soc. Chem. Ind.*, 1919, 306A.]

W. P. S.

Estimation of Glycerol by means of the Specific Gravity and Boiling Point.

AD. GRÜN and TH. WIRTH (*Zeitsch. angew. Chem.*, 1919, **32**, i, 59—62).—According to various authorities, the specific gravity of pure glycerol varies by 0.0025 to 0.0030 for each 1% of water added, whilst the recorded values for pure glycerol itself vary up to 0.0110, which would correspond with about 3½% of water. The results obtained with samples of pure anhydrous glycerol by the authors were D_{15}^{15} 1.2653±0.0001, and were thus in agreement with those given by Gerlach (*Chem. Ind.*, **7**, 277), whose table must therefore be accepted as the most trustworthy. As was shown by Gerlach (*loc. cit.*), the boiling point of glycerol is lowered from 290° to 239° by the addition of 1% of water. In the determinations made by means of Schleiermacher's apparatus (A., 1891, 873), the boiling point of pure glycerol was found to be 283° to 284°, but this was proved to be due to the absorption of about 0.05% of water during the introduction of the glycerol into the capillary tube. The method affords the most trustworthy means of estimating small amounts of water in glycerol, and is applicable in the presence of organic and inorganic salts, such as sodium chloride, but cannot be used with crude glycerins containing polyglycerols. [See also *J. Soc. Chem. Ind.*, 1919, 295A.]

C. A. M.

Preparation of a Solution of Cupric Hydroxide in Sodium Hydroxide for the Detection and Estimation of Sugars.

ED. JUSTIN-MUELLER (*J. Pharm. Chim.*, 1919, [vii], **19**, 18—20).—A solution, which serves all the purposes of Fehling's solution, may be obtained by adding 20 c.c. of 10% copper sulphate solution to 100 c.c. of 33.69% sodium hydroxide solution; the solution remains clear when kept, and does not give a precipitate when heated.

W. P. S.

Analysis of Cows' Milk, Particularly the Estimation of Lactose. HANS SALOMON and RUDOLF DIEHL (*Ber. Deut. pharm. Ges.*, 1918, **28**, 493—498).—Analyses are recorded showing that the quality of cows' milk has not been affected by the poor iodder available lately in Germany. In the estimation of lactose, the preliminary removal of proteins, etc., by precipitation with copper sulphate and sodium hydroxide, is not always complete, especially in the case of milks which have been preserved by the addition of formaldehyde; the use of zinc sulphate, copper sulphate alone, or a mixture of asaprol (sodium β -naphthol- α -monosulphonate) and citric acid is recommended for the purpose. W. P. S.

A New Method for the Estimation of Oxalic Acid. HUGO KRAUSE (*Ber.*, 1919, **52**, [B], 426—432).—When oxalic acid is heated with acetic anhydride at 100°, it decomposes briskly and quantitatively into carbon monoxide and carbon dioxide. Performed in a tube fitted with a generator of carbon dioxide and a nitrometer filled with potassium hydroxide, the reaction may therefore be used for quantitative purposes. The only common organic acid which also gives carbon monoxide under these conditions is formic acid, although even this reacts more sluggishly.

For soluble oxalates, the material is first evaporated with an excess of hydrochloric acid, and the slightly moist residue is spread out on the walls of the tube by shaking during the evaporation. Insoluble oxalates are treated with a mixture of acetic anhydride and sulphuric acid (9:1), but the method is not so good in this case, as the mixture alone develops some insoluble gas, necessitating a "blank" experiment, nor is it specific for oxalic acid.

J. C. W.

Volumetric Method for the Estimation of Salicylic Acid in the Presence of Salicylaldehyde. R. BZRG (*Chem. Zeit.*, 1919, **43**, 129).—The method depends on the formation of a yellow coloration when a solution of salicylaldehyde is treated with a slight excess of free alkali; the aldehyde thus acts as an indicator. An ethereal solution containing salicylic acid and salicylaldehyde is extracted with several successive quantities of $N/20$ -sodium hydrogen carbonate solution, and the aqueous extract is titrated with $N/20$ -sulphuric acid, the solution being boiled after each addition of the acid to expel carbon dioxide. The end-point is denoted by the solution remaining colourless when boiled. [See, further, *J. Soc. Chem. Ind.*, 1919, May.] W. P. S.

Volumetric Method for the Estimation of Urea. Applicable to Urine, Blood, Serum, etc. GOLSE (*Bull. Soc. Pharm. Bordeaux*, 1918, **56**, 188; from *J. Pharm. Chim.*, 1919, [vii], **19**, 20—22).—The urea solution is treated with a definite quantity (an excess) of sodium hypobromite solution, and, after one minute, potassium iodide and acetic acid are added and the liberated iodine is titrated with thiosulphate solution. The same

volume of hypobromite solution is then treated separately with potassium iodide and acetic acid, and titrated. The difference between the two titrations is equivalent to the amount of urea present; 6 atoms of iodine correspond with 1 molecule of urea. In the case of urine, the urea is precipitated as a mercury compound by treating the urine with Patein's reagent and sodium hydroxide; the precipitate is collected, washed, dissolved in acetic acid, and the solution treated as described. Blood is clarified with trichloroacetic acid, filtered, the urea precipitated in the filtrate by means of Patein's reagent and sodium hydroxide, and the process continued as above. W. P. S.

Reduction of the Quantity of Humin Nitrogen Formed in the Hydrolysis of the Nitrogenous Constituents of Feeding-stuffs. H. C. ECKSTEIN and H. S. GRINDLEY (*J. Biol. Chem.*, 1919, **37**, 373—376. Compare A., 1915, ii, 598, and A., 1916, i, 623; ii, 119).—The authors have attempted to render the Van Slyke method for the determination of the chemical groups characteristic of the amino-acids of proteins applicable with greater accuracy than heretofore in the analysis of feeding stuffs. In the first place, the interference of some of the non-protein nitrogenous constituents, such as certain lipoids, pigments, betaines, amygdalin, alkaloids, and some amides has been obviated by completely extracting the food product first with ether and then with cold absolute alcohol. In the second place, a method has been perfected by which the percentages of the humin nitrogen formed in the hydrolysis of the nitrogenous constituents of feeding stuffs are reduced so that they compare favourably with those obtained for pure proteins. This is effected, firstly, by the extraction referred to above, after which insoluble carbohydrates are converted as far as possible into soluble carbohydrates by boiling with 0.1% hydrochloric acid. The greater part of the soluble proteins is separated before hydrolysis from the soluble carbohydrates by neutralising the mineral acid and precipitating with alcohol. The small portion of proteins remaining in solution is hydrolysed by boiling with 5% hydrochloric acid instead of 20%.

By this method, the humin nitrogen is represented by values approximately a third of those obtained by the direct method.

J. C. D.

The Indophenine Reaction. EDWARD WRAY (*J. Soc. Chem. Ind.*, 1919, **38**, 83—84t. Compare A., 1904, i, 337; 1905, ii, 779).—A green coloration instead of blue is obtained in this reaction unless a small quantity of an oxidising substance, preferably nitric acid, is present. The test is made as follows: 25 c.c. of a 0.05% isatin solution in pure sulphuric acid are placed in a stoppered cylinder, and 1 c.c. of the benzene to be tested for thiophen is added, followed by 25 c.c. of sulphuric acid containing one drop of nitric acid; a blue coloration appears when the mixture is shaken.

W. P. S.

General and Physical Chemistry.

Relation between Intensity of Tyndall Beam and Size of Particles. RICHARD C. TOLMAN, ROSCOE H. GERKE, ADIN P. BROOKS, ALBERT G. HERMAN, ROBERT S. MULLIKEN, and HARRY DE W. SMYTH (*J. Amer. Chem. Soc.*, 1919, **41**, 575—587).—The intensity of the Tyndall beam in rosin smokes has been investigated further by the method previously described (this vol., ii, 180). In the case of smoke, since the particles are not of uniform size, no attempt was made to measure the size of the particles, but the results show that for the range of particles 10^{-6} — 10^{-4} cm., the Tyndall-meter reading increases with increased dispersion. Suspensions of silica particles in water were prepared, and the intensity of the Tyndall beam in these suspensions investigated. The particles were of uniform size and varied in the different suspensions from 10 — 260×10^{-5} cm. The Tyndall-meter readings in the case of silica suspensions increase with decreasing diameter of the particles. The results show that the readings are closely proportional to the reciprocal of the diameter of the particles. The relationships between the readings (T) and size of the particles are given by the equations $T = knd^6$ for very small particles and $T = k^1nd^2$ for large particles; d is the diameter of the particles, n the number of particles per c.c., and k and k^1 are constants. When the total concentration of the suspensions is given by c ; $c \propto nd^3$, hence the equations may be written $T = kcd^3$ and $T = k^1c/d$.
J. F. S.

Absorption by Troubled Media. Application to the Estimation of Suspensions. CHARLES CHÉNEVEAU and RENÉ AUDUBERT (*Compt. rend.*, 1919, **168**, 766—768).—The authors deduce the formula $1 - I/I_0 = e^{-B/M^\beta}$, where I/I_0 is the coefficient of transmission of light of the fine suspension, M is the total mass of particles, and B and β are two constants dependent only on the nature of the particles in suspension and the wave-length of light used. The accuracy of this formula has been verified for certain heterogeneous suspensions of mastic and for suspensions of silver chloride and barium sulphate. This thus provides a method of determining the amount of material in suspension providing there is no immediate sedimentation.
W. G.

Conductivity and Absorption of Sodium Vapour. ADOLFO CAMPETTI (*Nuovo Cim.*, 1918, [vi], **16**, ii, 115—138).—The results of the author's experiments show that, in unsaturated sodium vapour kept in the dark and freed from electrons emitted from the surface of the fused metal, spontaneous ionisation in the volume of the vapour occurs at high temperature; this ionisation becomes clearly manifest above 400° without marked dissymmetry as regards

the sign of the disperse charge. Such conductivity in the volume of the vapour is closely connected with the commencement of the absorption of the *D*-line, which under the above conditions is observed only at about 430°, but then persists when the temperature falls considerably. The cause of the appearance of absorption at somewhat lower temperatures under the ordinary conditions of observation is clearly shown to be the presence of electrons either given off from the surface of the molten metal or arising from the atoms of the metal in the state of vapour as a result of photo-electric action. It appears probable that the emitting or absorbing vibrators in sodium vapour are, for the *D*-line, the positive atom ions.

T. H. P.

Spectrum of Neon. K. W. MEISSNER (*Ann. Physik*, 1919, [iv], **58**, 333—374).—The red and infra-red spectrum of neon has been investigated by the interferometric method of Fabry and Perot (*Ann. Chim. Phys.*, 1897, [vii], **12**, 459), and also by means of a concave grating of 1 metre radius. Some seventy-five lines are recorded between the wave-lengths 7051.314 and 9840.42 Å.U., and in all cases the vacuum wave-length is calculated. The wave-lengths of the present measurements, together with those of previous measurements of the other portions of the spectrum, are examined with the object of arranging them in series, and the relationships of the eight series groups calculated.

J. F. S.

The Constitution of the Atom and the Properties of Band Spectra. H. DESLANDRES (*Compt. rend.*, 1919, **168**, 861—868).—Vegard's work (compare A., 1918, ii, 93, 94, 144) gives data concerning the inner rings of electrons adjacent to the nucleus, and the author considers that a study of band spectra may throw some light on the composition of the outer rings. The edges of the bands, which form the structure of the spectra, are given by $\nu = B(n + \beta)^2/2 - C(p + \gamma)^2/2 + K$, where *B*, *C*, *K*, β , and γ are constants, *n* and *p* being successive whole numbers.

The three types of spectra, line, band, and X-ray, are due to the action, more or less strong, of ions and electrons which encounter the atom. If the electron which arrives is very rapid, it penetrates to the nucleus and disarranges the ring nearest to the nucleus, causing it to lose an electron and giving rise to X-rays. If the electron is less rapid, only an outer ring is disarranged, and the line spectrum results. If, however, the velocity of the approaching electron is still less, the atom is only deformed and emits the band spectrum.

W. G.

The Verification of Bohr's Atomic Theory of Optical Spectra by Investigations of the Non-elastic Collisions of Slow Electrons with Gas Molecules. J. FRANCK and G. HERTZ (*Physikal. Zeitsch.*, 1919, **20**, 132—143. Compare *ibid.*, A., 1914, ii, 515; 1916, ii, 461).—The principle that for the monatomic gases without affinity for electrons the electrons are reflected from the

atoms with perfect elasticity up to a critical velocity of collision, when they lose their total energy of translation and give rise to radiation, has been found to be in complete accord with Bohr's theory. The critical energy of the electron in the case of mercury vapour, derived from a potential difference of 4.9 ± 0.1 volt, is equal to $h\nu$, where h is the quantum and ν the frequency corresponding with 2536 \AA. in the ultra-violet spectrum of mercury. The absorption and emission lines can be excited by free electrons, which suffer a loss of energy of $h\nu$ on collision. For normal, not excited, atoms, the change of the electron from one steady orbit to another corresponds with the absorption spectrum series. The limit of frequency of the series in the ultra-violet multiplied by the quantum h gives the work done in ionising the atom, and the limit may be calculated from the ionising potential and vice versa. The investigation of inelastic electronic collision and its attendant light emission gives a new means of analysing the lines of a spectrum into series and determining their relation. F. S.

Explanation of the Röntgen Spectrum and the Constitution of the Atom. L. VEGARD (*Physikal. Zeitsch.*, 1919, **20**, 97—104).—A theoretical paper in which the main results of previous publications are summarised (A., 1918, ii, 93, 94, 144). A generalised frequency formula is developed on the basis of the preceding work, and this is tested by comparison of curves produced from results calculated by this formula with the corresponding experimental curves. J. F. S.

X-Ray Spectroscopy. The L-Absorption Spectrum of Radium. M. DE BROGLIE (*Compt. rend.*, 1919, **168**, 854—855).—The L-absorption band of radium has been obtained by passing a beam of X-rays through a glass capillary tube containing solid radium sulphate. The tube is fixed before the spectroscope slit. The wave-length $\lambda = 0.659 \times 10^{-8} \text{ cm.}$ is found for this band, and calculations from this value lead to 88 as the atomic number of radium. J. F. S.

Crystalline Structure of Alums and the Rôle of Water of Crystallisation. L. VEGARD (*Ann. Physik*, 1919, [iv], **58**, 291—296).—Polemical against Schaefer and Schubert (A., 1916, ii, 505). The author shows that the measurements of Schaefer and Schubert do not prove that water of crystallisation occurs as a structural component in the grating system, and that the claim for priority made by these authors is unfounded. J. F. S.

Optical Investigation of the Constitution of some Oxygen Acids of Chlorine and Bromine and of their Esters and Salts. KONRAD SCHAEFER and WILLY KÖHLER (*Zeitsch. physikal. Chem.*, 1919, **93**, 312—324).—The absorption spectra of a number of the oxygen acids of the halogens, their esters, and salts have been measured. In the case of hypochlorous acid, ethyl hypo-

chlorite, and several metallic hypochlorites it is shown that the acid and ester have identical absorption spectra, but when the acid is completely neutralised by sodium hydroxide, the absorption spectrum changes in the sense that a deep, well-defined, broad band appears. Incomplete neutralisation gives an absorption spectrum which indicates both acid and salt. The author puts forward the formula $\text{Cl}\cdot\text{OH}$ and $\text{Cl}\cdot\text{OEt}$ for the acid and ester respectively, and $\text{Cl}\cdot\text{O}\cdot\text{Na} \rightleftharpoons \text{Cl}\cdot\text{O} + \text{Na}^+$ for the salt. Hypo-

bromous acid and sodium hypobromite give absorption spectra similar to those of the corresponding chlorine compounds. Solutions of chlorine dioxide, chlorous acid, and several chlorites were also examined. Gaseous chlorine dioxide shows a broad band and a large number of narrow bands, whilst on solution the bands are broadened and many run together, but in general the region of absorption remains the same. The maximum of absorption is at 2900, and the minimum at the frequency 3800. These results indicate that there is little formation of chloric or chlorous acid on solution. On neutralisation, the band disappears, so that the chlorites have a different constitution from the acid, the formulæ $\text{O}=\text{Cl}\cdot\text{OH}$ and $\text{Cl}\cdot\text{O}\cdot\text{M}$ being suggested in the two cases. Bromic

acid, iodic acid, and their alkali salts were also investigated. The only difference observed in these cases was the shifting of the terminal absorption toward higher frequencies in the case of the bromine compounds. The measurements show that the constitution of these acids is probably that of a true acid, as distinguished from a pseudo-acid. J. F. S.

Use of Einstein's Photochemical Equivalent Law. I. W. NERNST (*Zeitsch. Elektrochem.*, 1918, **24**, 335—336).—A theoretical paper in which the reason for the inapplicability of the Einstein photochemical law to the photosynthesis of hydrogen chloride is put forward. The primary action of light is the splitting of the chlorine molecule, this then reacts $\text{Cl} + \text{H}_2 = \text{HCl} + \text{H} + 25,000$ cal., and the hydrogen atom thus produced reacts with a chlorine molecule, $\text{H} + \text{Cl}_2 = \text{HCl} + \text{Cl} + 19,000$ cal. This explains why so much more hydrogen chloride is produced than corresponds with the requirement of the Einstein law. This also explains the negative catalytic effect of impurities on this reaction. The chlorine and hydrogen atoms are very reactive substances, and consequently will be removed from the reaction system by their combination with the impurities. This view is confirmed by the limited reaction when bromine vapour and hydrogen are illuminated, for, as the equation $\text{Br} + \text{H}_2 = \text{HBr} + \text{H} - 15,000$ cal. shows, hydrogen is not a suitable acceptor for bromine.

J. F. S.

Use of Einstein's Photochemical Equivalent Law. II. LOTTE PUSCH (*Zeitsch. Elektrochem.*, 1918, **24**, 336—339. Compare preceding abstract).—The reaction between bromine vapour

and hydrogen in the presence of toluene, hexane, and heptane when exposed to light has been investigated. The results confirm the view put forward in the preceding paper that in the case of chlorine and hydrogen the primary reaction is strictly in accordance with the Einstein law, and that the secondary reactions account for the extremely large quantities of hydrogen chloride produced.

J. F. S.

The Possibility of Separating Isotopes. F. A. LINDEMANN and F. W. ASTON (*Phil. Mag.*, 1919, [vi], **37**, 523—534).—The possible methods of separating isotopes, distillation, to which, thermodynamically, chemical separation is closely allied, diffusion, density, and positive rays, are discussed theoretically. The conclusion is reached that separation by distillation and chemical methods ought to be possible under appropriate conditions, although the separation may be small. None of the possible physical methods holds out any prospect of effecting an easy separation, centrifugal separation being the most promising. For neon and meta-neon, with a peripheral velocity of 10^5 cm. per second, it is calculated that the apparent atomic weight of the gas at the edge should be 1.0065 times that of the gas at the centre, and for thorio- and uranio-lead a nearly 50% increase in the concentration of the former at the edge might result.

Experiments are described on the fractionation of atmospheric neon by charcoal at liquid air temperature. After about 3000 fractionations, in which the gas was divided into seven main fractions, the density as determined by the quartz micro-balance was unchanged.

F. S.

Protactinium and the Life Period of Actinium. OTTO HAHN and LISE MEITNER (*Physikal. Zeitsch.*, 1919, **20**, 127—130. Compare *ibid.*, A., 1918, ii, 345; Soddy and Cranston, A., 1918, ii, 211).—Evidence of the period of actinium obtained from the proportionate increase of the α -radiation of protactinium preparations with time confirms the value obtained directly from the rate of decay of the radiation of actinium preparations. From the known ranges of the six α -rays involved in the protactinium-actinium series, the ratio of the initial ionisation produced by a thin film of protactinium to that when the actinium and its products are in equilibrium with the protactinium is calculated to be 1:5.74. From the proportionate increase of α -radiation of five preparations over periods from 400 to 600 days, a half-period of actinium of twenty years is deduced. This indicates that in the carbon tetrachloride sublimation of Soddy and Cranston less than 1% of the eka-tantalum (protactinium) in the mineral was separated. The value found from the decay curve of the radiation of actinium over seven years gives for the half-period of actinium twenty years ($\pm 10\%$). This corresponds with a period of average life of 28.8 years.

F. S.

Chemical Action produced by Radium Emanation. I. Combination of Hydrogen and Oxygen. S. C. LIND (*J. Amer. Chem. Soc.*, 1919, **41**, 531—551).—The velocity of combination of hydrogen and oxygen under the influence of radium emanation has been investigated. The experiments were effected in spherical and cylindrical bulbs of varying size by a method which is a slight modification of that of Cameron and Ramsay (T., 1908, **93**, 966—992). It is shown that the velocity of reaction in a given volume is dependent on two variables only, the quantity of emanation, E , and the gas pressure, P . The velocity constant obtained by integration of the equation arising from this assumption has been verified. It has the form $(\log P/P_0)/E_0(e^{-x} - 1) = \text{const.}$ The effect of increasing the spherical volume is to diminish the velocity constant (expressed in terms of pressure) according to the equation $84.1/D^2 = \text{const.}$, where D is the diameter in cm. This is to be expected from the increase of the average path of the α -particle proportional to D , whilst the pressure effect diminishes proportionally to D^3 . The above formula is applicable only to globes in which the size of the shortest α -ray is not exceeded by the diameter. Varying proportions of hydrogen and oxygen change the velocity in the way which is to be expected from the change produced in the specific ionisations. Excess of oxygen gives a velocity higher than normal, which increases as the proportion of oxygen increases. Excess of hydrogen produces the opposite effect. The temperature-coefficient of the reaction between 0° and 25° is zero, as would be expected from ionisation. Calculation of the ionisation by the method of average path of the α -particles shows that for each pair of ions produced in the gaseous mixture, 3.9 molecules of water are formed; this value agrees fairly well with 3.7 found by Schuer (A., 1914, ii, 762). The reaction in cylindrical volumes obeys the same laws as that in spherical volumes, which would appear to confirm the author's original contention that the average path in a cylinder is the same as in a sphere of equal volume (*Amer. Electrochem. Trans.*, **34**).

J. F. S.

Chemical Action produced by Radium Emanation. II. Chemical Effect of Recoil Atoms. S. C. LIND (*J. Amer. Chem. Soc.*, 1919, **41**, 551—559. See preceding abstract).—The action of radium emanation in causing the combination of electrolytic hydrogen and oxygen is abnormally high in small spheres, particularly at low gaseous pressures. The action is shown to be six to seven times greater than that due to the normal α -ray effect. This abnormally high velocity is explained by the assumption that the recoil atoms contribute to the reaction in proportion to their relative ionising power. The results of the author's calculations and experiments are in general agreement with Wertenstein's ionisation data for recoil atoms (A., 1914, ii, 514).

J. F. S.

Determination of the Ionisation Potential for Electrons in Helium. FRANK HORTON and ANN CATHERINE DAVIES (*Proc. Roy. Soc.*, 1919, [A], **95**, 408—429).—The ionisation potential of

electrons generated by a heated tantalum wire in helium of low pressure has been experimentally determined. The experiments show that radiation occurs when electrons having a velocity of about 20.5 volts collide with helium atoms, and that this is not accompanied by any ionisation of the gas. It is also shown that ionisation of the helium occurs when the velocity of the electrons is raised to about 25.7 volts, and that no other type of radiation is produced at this point. The potential values were obtained from an accurate investigation of the position of the bends of the current-potential difference curves over a range of 2—3 volts in the neighbourhood of the value. The mean values from these experiments were 20.4 volts and 25.7 volts respectively. By a method in which the value of V_3 was made zero, and the electrons could produce radiation or ionisation over longer paths, the mean values 20.45 volts and 25.5 volts were obtained. It may be taken that 20.4 volts represents the minimum radiation potential and 25.6 volts the minimum ionisation potential. These values confirm Bohr's suggestion that radiation, and not ionisation, occurs at about 20 volts, but the value found for the ionisation potential is considerably lower than the value, 29 volts, deduced from Bohr's theory of the structure of the helium atom. J. F. S.

Molecular Electric Field in Gases. P. DEBYE (*Physikal. Zeitsch.*, 1919, **20**, 160—161).—A theoretical paper in which calculations, based on the Stark hypothesis that the broadening of spectral lines is to be attributed to a molecular electric field, are made by which the approximate dimensions of the molecular electric field are calculated. Assuming that the charge of an electron is $5 \times 10^{-10} \text{ g.}^{\frac{1}{2}} \text{ cm.}^{\frac{1}{2}} \text{ sec.}^{-1}$ (electrostatic units), and the radius of the molecule is 10^{-8} cm. , it is shown that the charge on a charged molecule or ion may be taken as $5 \times 10^{-10} \text{ g.}^{\frac{1}{2}} \text{ cm.}^{\frac{1}{2}} \text{ sec.}^{-1}$, and in the case of an uncharged molecule which bears an electric moment, this may be put at $5 \times 10^{-18} \text{ g.}^{\frac{1}{2}} \text{ cm.}^{\frac{1}{2}} \text{ sec.}^{-1}$. If the electric moment disappears, the electric moment of inertia is then calculated to $5 \times 10^{-26} \text{ g.}^{\frac{1}{2}} \text{ cm.}^{\frac{1}{2}} \text{ sec.}^{-1}$. Values of the above dimensions have been recently obtained by Jona (this vol., ii, 130). The value of the field strength due to the ions (F_1) is given by $F_1 = en^{\frac{2}{3}}$, where e is the ionic charge and n the number of gas molecules per cubic centimetre. The field strength, F_2 , due to uncharged molecules which have an electric moment, is given by $F_2 = mn$, where m is the electric moment, and for the case where the electric moment is zero and only an electric moment of inertia present. $F_3 = \Theta n^{\frac{1}{3}}$ gives the field due to this cause, where Θ is the electric moment of inertia. Substituting the appropriate data $F_1 = 4500$ electrostatic units = 1,350,000 volts/cm., $F_2 = 135$ electrostatic units = 40,500 volts/cm., and $F_3 = 4$ electrostatic units = 1200 volts/cm. In the case of ammonia and sulphur dioxide, the electric moment is actually of the above order, and an electric field of 4×10^4 volts/cm. is existent. J. F. S.

Electromotive Activity of Carbon Monoxide. FRIEDRICH AUERBACH (*Zeitsch. Elektrochem.*, 1919, **25**, 82—84).—A theoretical paper in which the activity of carbon monoxide in electromotive processes is considered. It is shown that the *E.M.F.* given by Hofmann (this vol., ii, 8) for the element O_2/CO may not be directly compared with that calculated from the free energy of the reaction $2CO + O_2 \rightleftharpoons 2CO_2$, because in alkaline electrolytes carbon monoxide is not burnt to carbon dioxide, but to carbonate. In the present calculations, the *E.M.F.* is much smaller than that observed by Hofmann. J. F. S.

A Modified Hydrogen Electrode. J. HUDIG and W. STURM (*Chem. Weekblad*, 1919, **16**, 473—481).—In their measurements of the hydrogen-ion concentration of aqueous soil extracts by means of the hydrogen electrode, the authors experienced difficulty in obtaining constant results for any one extract, even after filtration of the latter through an ultra-filter. Whilst no explanation of the observed fluctuations in *E.M.F.* is suggested, it is found possible to obtain satisfactory constancy in the readings by the following modifications in the construction and use of the hydrogen electrode. The electrode consists of a platinum gauze cylinder platinised over a gold coating. The soil suspension is contained in a closed vessel, through the stopper of which pass the electrode, gas inlet and outlet tubes, electrolyte tube, and a stirring gear motor driven through a mercury seal. A rapid stream of hydrogen is supplied both to the inner and to the outer surface of the gauze cylinder during the measurement, whilst soil and liquid are kept in intimate contact by vigorous stirring. W. S. M.

The Theory of Electrolytic Ions. IX. Space-filling and Mobility of Univalent Organic Ions. R. LORENZ (*Zeitsch. anorg. Chem.*, 1919, **105**, 175—186).—The author has calculated the space-filling numbers of more than one hundred univalent organic cations, containing from 6 to 44 atoms (compare A., 1918, ii, 303). The space-filling number ψ is the ratio of two volumes, ϕ/V , where ϕ is the ionic volume calculated from the ionic mobility and V is the volume derived from the density or from Kopp's formula. The ion radius, r , is given by the formula $r = 1/u \times 8.954 \cdot 10^{-7}$. In the series of ions examined, this radius is found to be a linear function of the number of atoms in the ion. Hevesy (A., 1916, ii, 594) has advanced the theory that the ions in solution endeavour to attain an approximately constant potential, which, in the case of water, is about 70 millivolts. The normal radius of an ion charged to this potential he calculates to be 2.8×10^{-8} cm. To adjust their potential, the smaller ions, he supposes, increase their radius by becoming hydrated, thereby lowering their mobility. In the series of ions under examination, this "normal" radius, corresponding with a "normal" mobility, is reached with not fewer than 27 atoms in the ion. According to Hevesy's theory, ions with fewer than 27 atoms should become

hydrated to bring their radii and mobilities to the "normal" value. There is no evidence that they do become so hydrated, however, for the relation between the number of atoms and the ionic radius is linear, and there is no discontinuity in the curve at about 27 atoms. Further, there is very little difference between the mean values of the space-filling numbers with more than 27 atoms ($\psi=0.474$) and the mean of all ions with from 6 to 44 atoms ($\psi=0.388$). For the "ideal" organic cation containing between 4 and 50 atoms, the value of the space-filling number can be taken as 0.40.

E. H. R.

Movement of the Ions during Electrolysis. CARLO DEL LUNGO (*Nuovo Cim.*, 1918, [vi], 16, ii, 173—181).—By application of Stokes's law to the question of the movement of the ions, the author deduces theoretically Walden's empirical law, according to which, for one and the same electrolyte, the product of the viscosity of the solvent and of the equivalent conductivity, Λ_0 , is a constant magnitude independent of the temperature. It is found also that the variation of the conductivity, Λ_0 , should depend solely on the variation of the viscosity-coefficient, η , as it may be assumed that, at least within certain limits, change of temperature does not sensibly influence the diameters of the ions. Consequently, the temperature variation of Λ_0 should be virtually the same for all electrolytes in aqueous solution. Not only is the law in general verified for salts, but the temperature-coefficients of conductivity between 18° and 40° have the limiting values $2.3 \cdot 10^{-12}$ and $2.6 \cdot 10^{-12}$, which correspond closely with the temperature-coefficient of the viscosity of water.

Stokes's law allows also of calculation of the diameter of the ions, and the values thus derived are in good agreement with those deduced in accordance with the kinetic theory of gases. In general, the ions are small in comparison with the molecules, but the difference is exceptionally marked with the ions H^+ and OH^- , the diameters of which are only about one half of what they should be according to the diameters of the molecules H_2 , O_2 , and H_2O . The existence of free H^+ and OH^- ions in all aqueous solutions, and perhaps in greater number in solutions of acids and bases, would cause the calculated velocities of the ions of the electrolyte to be greater than the true values; these considerations would explain the exceptionally high values obtained for the transport velocities of the ions H^+ and OH^- and the low values of the corresponding temperature-coefficients, and of the diameters calculated according to Stokes's law. It appears that the ions H^+ and OH^- exist under special conditions different from those shown by other ions, and that the friction between them and water molecules is far less than with other ions.

The dimensions of the ions of the metals and of the non-gaseous non-metals given by Stokes's law are compared with those calculated on the basis of the atomic volumes. The agreement is good for univalent elements, with the exception of potassium, but there

is a moderately high and approximately constant difference in the case of the bivalent metals. T. H. P.

The Decomposition of Dielectric Liquids in the Midst of which an Arc passes. ED. URBAIN and CLAIR SCAL (*Compt. rend.*, 1919, **168**, 887—889).—An arc, started by a high-frequency spark, and continued by a current at low voltage, in passing through the tetrachloride of titanium, tin, or carbon, causes a marked decomposition, chlorine being liberated. With saturated liquid hydrocarbons, there is a liberation of acetylene, ethylene, and hydrogen, and a deposition of carbon. With pinene, the same products are obtained, and at the same time there is a marked formation of isoprene in the liquid. Ketones yield carbon monoxide and different hydrocarbons. In the case of organic dielectric liquids, the process of decomposition differs according as the liquid is maintained at 15° or at its boiling point, the decomposition being far more thorough in the latter case. W. G.

Thermochemical Application of the Grating Theory. M. BORN (*Ber. Deut. physikal. Ges.*, 1919, **21**, 13—24).—A theoretical paper in which it is shown that the formation or decomposition of a crystalline substance must be accompanied by a heat change which is equal to the electrical energy of the grating. It is impossible to calculate this quantity with the hope of finding agreement between the experimental quantity and the calculated quantity of heat, but it is shown in the case of the alkali halogen salts, and also for the calcium halogen salts, that the order of the two quantities is the same. The formation of a crystal of sodium chloride from its elements is considered as occurring in three steps: (1) the subdivision of sodium into isolated atoms and the ionisation of these, which uses a quantity of work Z_{Na} ; (2) the subdivision of the chlorine into atoms and the ionisation of these, which absorbs work Z_{Cl} ; (3) the combination of the ions of sodium and chlorine to form the solid crystal, whereby the electrostatic crystal energy, U_{NaCl} , is obtained as heat. The heat of formation is then given by $Q_{NaCl} = -Z_{Na} - Z_{Cl} + U_{NaCl}$. It is shown that $\Delta Z_{Na,K} = Z_{Na} - Z_K = U_{NaCl} - U_{KCl} - Q_{NaCl} + Q_{KCl}$ and from this $\Delta Z_{Na,K}$ is independent of the halogen. The value of U is calculated for the lithium haloids, and found to fall from the fluoride to the iodide.

J. F. S.

Thermal Conductivity of Organic Compounds. W. HERZ (*Zeitsch. physikal. Chem.*, 1919, **93**, 376—379).—A theoretical paper in which the relationship between the density (d), specific heat (c), and the thermal conductivity (k), as expressed in the equation $k = \eta \cdot c \cdot d$, is considered. It is shown that the quantity k/cd decreases in homologous series of organic compounds with increasing molecular weight and also with increasing molecular diameter. This is in keeping with the assertion of Weber (*Sitzungsber. K. Akad. Wiss. Berlin*, 1885, 809) that this quantity is

inversely proportional to the mean distance between the molecules. The heat capacity ($c.d$) for equal volumes of liquids and the thermal conductivity k are proportional to one another, although many exceptions to this occur. In some liquids, the heat capacity varies inversely as the thermal conductivity. J. F. S.

Equation of State for Liquids and Vapours. I. Vapour Phase of Ethyl Ether. FREDERICK G. KEYES and WILLIAM A. FELSING (*J. Amer. Chem. Soc.*, 1919, **41**, 589—619).—The authors discuss the basal ideas of the kinetic theory in their relationship to the work of van der Waals, and they deduce an equation of state on the present-day conception of the atom. This equation has the form $p = RTx/(v-\delta) - Ax/(v-l)^2$, in which $\delta = \beta e^{-\alpha/v}$ (see *Proc. Nat. Acad. Sci.*, 1917, **3**, 323). It is shown that the strict proportionality between the pressure increment and the temperature increment at constant volume is the only trustworthy test of a system with one molecular type, and that divergence from the linear curve is due to polymerisation or change in the molecular system. The data of Ramsay and Young and other investigators for ethyl ether have been re-calculated on the above formula, and it is shown that the particular form of the mathematical function $\delta = \beta e^{-\alpha/v}$ and the cohesive pressure expression $\phi = A/(v-l)^2$ are both exact. The pt curves for ether have been measured at constant volume, and are shown to be linear within the limits of accuracy of the measurements. From the constants of these curves, the δ -equation and the ϕ -equation have been computed, and the mathematical form deduced for each shown to be exact. Amagat's data have been used to determine the equation for δ (liquid phase) on the assumption that this phase is bimolecular. The ratios of the β - and α -constants have been compared and found to be simple. For one molecule of liquid, the limiting volume correction β_2 is numerically equal to the limiting volume correction of the gas β_1 , whilst α_2 is only one half as great as α_1 . J. F. S.

Specific Heat and Latent Heat of Fusion of the Dichloro-, Chlorobromo-, Dibromo-, Bromiodo-, and Di-iodo-benzenes.

I. J. NARBUTT (*Zeitsch. Elektrochem.*, 1918, **24**, 339—342).—The specific heat and latent heat of fusion of a number of dihalogenated benzenes have been determined. The following numerical results have been obtained: c' is the mean specific heat of the molten substance, c the mean specific heat of the solid, and g the latent heat of fusion. (1) *p*-Dichlorobenzene, $c'_{t_2} = 0.22024 + 0.0003462(t_1 + t_2)$, c' between 99.1° and 52.9° is 0.298 ± 0.004 , $g = 29.50 \pm 0.11$ cal.; *o*-dichlorobenzene, $c = 0.185 \pm 1\%$ between -21.3° and -75.6° , $c'_{t_2} = 0.27022 + 0.0001512(t_1 + t_2)$, $g = 21.01 \pm 0.14$ cal.; *m*-dichlorobenzene, $c = 0.186 \pm 1\%$ between -27.8° and -76.2° , $c'_{t_2} = 0.27022 + 0.0001512(t_1 + t_2)$, $g = 20.47 \pm 0.14$ cal.; *p*-chlorobromobenzene, $c' = 0.239 \pm 0.004$ between 99.8° and 64.6° ,

$c_{t_2}^{t_1} = 0.17066 + 0.0002499(t_1 + t_2)$, $g = 23.42 \pm 0.09$ cal.; *o*-chlorobromobenzene, $c_{t_2}^{t_1} = 0.21497 + 0.0001174(t_1 + t_2)$, $c = 0.192 \pm 1\%$ between -15.1° and -74.8° , $g = 15.44 \pm 0.11$ cal.; *m*-chlorobromobenzene, $c' = 0.199 \pm 2\%$ at -75.8° , $c_{t_2}^{t_1} = 0.21224 + 0.0001174(t_1 + t_2)$, $g = 15.34 \pm 0.10$ cal.; *p*-dibromobenzene, $c_{t_2}^{t_1} = 0.13934 + 0.0001907(t_1 + t_2)$, $g = 20.84 \pm 0.08$ cal.; *o*-dibromobenzene, $c_{t_2}^{t_1} = 0.17994 + 0.0001070(t_1 + t_2)$, $c = 0.248 \pm 0.75\%$ between 0° and -73.2° , $g = 12.79 \pm 0.10$ cal.; *m*-dibromobenzene, $c_{t_2}^{t_1} = 0.17535 + 0.0001070(t_1 + t_2)$, $c = 0.134 \pm 1\%$, $g = 13.39 \pm 0.09$ cal.; *p*-bromoiodobenzene, $c_{t_2}^{t_1} = 0.11627 + 0.0001576(t_1 + t_2)$, $g = 16.57 \pm 0.07$ cal.; *o*-bromoiodobenzene, $c_{t_2}^{t_1} = 0.15285 + 0.0000666(t_1 + t_2)$, $c' = 0.148 \pm 2\%$ between 0° and -75.5° , $g = 12.2 \pm 2\%$; *m*-bromoiodobenzene, $c_{t_2}^{t_1} = 0.15134 + 0.0000666(t_1 + t_2)$, $c = 0.143 \pm 1\%$ between -12.5° and -74.8° , $g = 10.30 \pm 0.10$ cal.; *p*-di-iodobenzene, $c_{t_2}^{t_1} = 0.10093 + 0.0001332(t_1 + t_2)$, $g = 16.21 \pm 0.10$ cal.; *o*-di-iodobenzene, $c_{t_2}^{t_1} = 0.13574 + 0.0000388(t_1 + t_2)$, $g = 10.20 \pm 0.05$ cal.; *m*-di-iodobenzene, $c_{t_2}^{t_1} = 0.10093 + 0.0001332(t_1 + t_2)$, $c' = 0.140 \pm 0.002$ between 99.6° and 34.2° , and 0.137 ± 0.003 between 63.2° and 34.2° , $g = 11.55 \pm 0.03$ cal. The trustworthiness of the formulæ is tested by calculation of the mean specific heat for each set of experimental conditions, and the results in each case are well in accordance with the experimental values.

J. F. S.

Specific Heat and Latent Heat of Fusion of the Dichloro-, Chlorobromo-, Dibromo-, Bromoiodo-, and Di-iodo-benzenes.

II. J. NARBUTT (*Zeitsch. Elektrochem.*, 1918, **24**, 342—354. Compare preceding abstract).—A theoretical paper in which the results recorded in the previous paper are discussed. The specific heats of the liquid isomerides of the dihalogenated benzenes are practically the same, whereas theoretically they could differ somewhat. The specific heat of very strongly supercooled dihalogenated benzenes changes according to the same rule as is followed above the freezing point. A formula is deduced for calculating the specific heat of nearly related non-associated compounds. This formula has been tested in the case of the dihalogenated benzenes. The dihalogenated benzenes, according to the rule of Longinescu (*A.*, 1908, ii, 931), are non-associated. The critical temperature and the critical volume of several of the dihalogenated benzenes have been calculated; the following values are recorded, which are the mean of the values of the three isomerides: dichlorobenzene, T_k 689° , ϕ 2.43; chlorobromobenzene, T_k 725° , ϕ 1.95; dibromobenzene, T_k 760° , ϕ 1.65; bromoiodobenzene, T_k 809° , ϕ 1.45; chloroiodobenzene, T_k 774° , ϕ 1.66; and di-iodobenzene, T_k 858° .

J. F. S.

Specific Heat and Latent Heat of Fusion of the Dichloro-, Chlorobromo-, Dibromo-, Bromoiodo-, and Di-iodobenzenes. III. J. NARBUTT (*Zeitsch. Elektrochem.*, 1919, 25, 51—57. Compare preceding abstracts).—A theoretical consideration of the results recorded in part I. It is shown that the latent heat of fusion of the dihalogen benzenes decreases in general with increasing molecular weight and decreases with increasing melting point. The mean value of the quotient of the molecular latent heat, M , and the absolute melting point, T , $M/T = \phi$, has the value 13.3 for the para-series, 11.8 for the ortho-series, and 12.0 for the meta-series. The mean values do not differ very much from the individual values, consequently the latent heat of fusion can be calculated for those cases where it has not been experimentally determined. The eutectic points of the system *p*-dichlorobenzene-*p*-di-iodobenzene have been calculated and found to correspond closely with the experimental values. In some cases, the maximum work of solidification has been calculated from the data obtained for the supercooled liquids. The difference between the molecular volumes in the liquid and solid state has been calculated for several of the dihalogenated benzenes. In the case of the para-dihalogenated benzenes, the quotient of molecular latent heat of fusion and the absolute melting point is three times as large as the difference between the molecular heats at the melting point, whilst it is equal to the difference of the mean molecular heats between the melting point and the absolute zero. J. F. S.

Specific Heat and Latent Heat of Fusion of the Dichloro-, Chlorobromo-, Dibromo-, Bromoiodo-, and Di-iodobenzenes. IV. J. NARBUTT (*Zeitsch. Elektrochem.*, 1919, 25, 57—66. Compare preceding abstracts).—A mathematical consideration of the experimental results recorded in part I. It is shown that in general the solid isomerides of the dihalogenated benzenes have practically the same specific heat over the temperature range examined, but in some cases a markedly different value is obtained. The dependence of the specific heat on the temperature is greater in the solid state than in the liquid state. The specific heat changes quite regularly with temperature even in the neighbourhood of the melting point. The mean specific heat cannot be calculated by the Neumann rule to nearer than 2% even when the dependence of this factor on temperature is taken into account. The value of β_0 of the Nernst and Lindemann formula has been calculated for the various atoms, and the following values obtained: C (attached to H) 3100, C (attached to a halogen) 1400, H (attached to C) 850, Cl (attached to C) 365, Br (attached to C) 250, and I (attached to C) 100. These values are, however, not trustworthy for calculations involving extrapolation to very low temperatures. The work of expansion against the cohesive forces is the same for the gram-molecule of the solid dihalogenated benzenes. J. F. S.

Latent Heats of Fusion and their Relation to Molecular Composition. HARBORD GEORGE WAYLING (*Phil. Mag.*, 1919, [vi], **37**, 495—497).—The latent heat of fusion multiplied by the molecular number (that is, the sum of the atomic numbers of the atoms in the molecule) and divided by the absolute melting point is for many compounds equal to the number of the atoms in the molecule. Thus for water $80 \times 10 \div 273 = 2.93$. For the majority of salts with water of crystallisation, the rule holds if two instead of three is allowed for the number of atoms in the water molecule. The generalisation holds for a number of inorganic salts and for formic acid and chloroform. Acetic acid, phenylacetic acid, and butyric acid all yield the same number, 5, but no simple connexion occurs for the closed-ring or aromatic compounds. F. S.

Cryoscopic Investigation of Double Salts and Complex Salts in Aqueous Solution. E. CORNEC and G. URBAIN (*Bull. Soc. chim.*, 1919, [iv], **25**, 131—136).—A more detailed account of work already published (compare A., 1914, ii, 428). W. G.

The Measurement of Very Low Temperatures. XXIX. Vapour Pressures of Oxygen and Nitrogen for obtaining Fixed Points on the Temperature Scale below 0°. P. G. CATH (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 656—663).—The vapour pressures of oxygen and nitrogen have been determined at temperatures in the neighbourhood of 57° to 90° (abs.). In the case of oxygen, the results can be expressed by the equation $\log p = A/T + B + CT$ (p in atm.), with $A = -419.31$, $B = 5.2365$, $C = -0.0648$. From this equation, the normal boiling point of oxygen would be 90.13° on Kamerlingh Onnes' scale, the actually observed value being 90.14°. The nitrogen results can be expressed by a similar equation, in which $A = -334.64$, $B = 4.6969$, and $C = -0.00476$. The boiling point of nitrogen calculated from the equation is 77.31° on the same scale. Measurements of the vapour pressure of solid nitrogen give the relation $\log p = -358.73/T + 4.7769$ as holding near the triple point. This equation gives for the triple point $T = 63.25^\circ$, $p = 0.1269$ atm., or 9.64 cm. E. H. R.

Vapour Pressure and Latent Heat of Vaporisation of Silicon Hydrides and their Simple Derivatives. ROBERT WINTGEN (*Ber.*, 1919, **52**, [B], 724—731. Compare Stock, Somieski, and Wintgen, A., 1918, ii, 110, 111).—A mathematical investigation of the data recorded by Stock and his co-workers on the vapour tension at various temperatures of simple silicon compounds, and the calculation of the molecular latent heat of vaporisation of the substances at any temperature. H. W.

Vapour Pressure Regularities. II. W. HERZ (*Zeitsch. Elektrochem.*, 1918, **24**, 333—335).—The proportionality factor of Dühring's rule has been calculated for the substances chlorine, bromine, iodine, argon, krypton, xenon, oxygen, sulphur, nitrogen,

phosphorus, arsenic, bismuth, copper, silver, zinc, cadmium, mercury, tin, lead, and a large number of organic substances. It is shown that in all cases it exhibits an approximate constant. In the case of the non-metals, the q value increases with increasing pressure, and in every group of the periodic system with increasing atomic weight. The metals behave in the opposite way. The q value for compounds in most cases exhibits a tendency to increase with increasing molecular weight in each group of the periodic system and in each homologous series of organic substances.

J. F. S.

Molecular Theory of the Vapour Pressure of Solid Substances and its Significance in the Calculation of Chemical Constants.

OTTO STERN (*Zeitsch. Elektrochem.*, 1919, **25**, 66—80).—A mathematical paper in which a theory of the vapour pressure of solid substances is developed on the basis of the following four hypotheses: (i) The attractive forces between atoms in the gaseous phase may be neglected on account of the relatively great distance between the atoms. (ii) The atoms exercise attractive forces on one another in the solid phase, and these forces are in equilibrium about the centres of gravity of the atoms. In the case of crystals, these forces are arranged orderly in the crystal grating. (iii) The atomic forces operate so that when an atom moves from its position of equilibrium, an opposing force is set up which tends to bring it back into the position of equilibrium. The magnitude of this force is proportional to the amount of movement of the displaced atom. (iv) To move an atom from its position of equilibrium, a definite finite amount of work, ϕ_0 , is necessary, so that $N\phi_0 = \lambda_0$ is the heat of sublimation at the absolute zero, on the assumption that at this point all atoms are in their equilibrium positions. Complicated formulæ are developed on these assumptions, and these take account of the different frequencies of the atoms. From these formulæ others are developed for calculating the chemical constants.

J. F. S.

Vapour Pressure of Acetone-Chloroform Mixtures.

ALFRED SCHULZE (*Zeitsch. physikal. Chem.*, 1919, **93**, 368—375).—The vapour pressure of various mixtures of acetone and chloroform has been determined at 30°, 70°, and 90°, and composition-pressure curves constructed for the three temperatures. The curves indicate that acetone-chloroform mixtures contain an equimolecular compound of the two constituents in a dissociated condition, which with increasing temperature apparently becomes less. At 30°, a distinct association of acetone is noticeable. By the aid of the law of mass action, the vapour pressure of the various mixtures was calculated, and the results shown to be in good agreement with the experimental values.

J. F. S.

Explosion, Implosion, and Bursting. WALTER BRIEGER and HANS SCHIMANK (*Zeitsch. Elektrochem.*, 1918, **24**, 354—356. Compare A., 1917, ii, 462).—A discussion on the exact definition of

the term explosion. An explosion is defined as the sudden development of a gaseous volume, an implosion as the sudden disappearance of a gaseous volume. Bursting may be occasioned by either process or by inequalities of pressure or strain. J. F. S.

Calculation of the Density of some Elements at the Absolute Zero. W. HERZ (*Zeitsch. anorg. Chem.*, 1919, **105**, 171—174).—The densities and atomic volumes of a number of elements at absolute zero have been calculated, making use of Lorenz's relation between the volume at absolute zero and that at the critical point, boiling point, and melting point (A., 1916, ii, 312). These relationships are given by the equations $d_0 = 1.41d_s = 3.75d_c = 1.21d_e = \bar{d}(0.77 + 0.64T/T_s)$, in which \bar{d} is the density, T is the absolute temperature, and the suffixes o , s , k , and e represent, respectively, absolute zero, boiling, critical, and melting points. The values of d_0 calculated from the different equations do not always show very good agreement; in the case of mercury, for instance, d_0 varies between 14.23 and 17.41. It is claimed, however, that in most cases a very fair approximation to the true value is obtained. Sodium (1.083) has a greater zero density than potassium (1.004), but in all other cases the density increases with the atomic weight. E. H. R.

Physical and Chemical Theories [of the Action of Toxins, Dyes, etc.]. I. TRAUBE (*Chem. Zeit.*, 1919, **43**, 129—130).—Polemical. A continuation of the controversy with Karrer (Traube, A., 1912, ii, 740; Karrer, A., 1918, ii, 431).

Measurement of the Thickness of Film formed on Glass and Sand. EARL PETTJOHN (*J. Amer. Chem. Soc.*, 1919, **41**, 477—486).—A method is described by which the thickness of a film of liquid, capable of forming on the surface of sand and glass beads without free liquid being present, may be measured. The method consists in placing a known weight of sand (200 grams) in a dry, conical flask and adding the liquid drop by drop from a burette with repeated shaking after each addition until particles of the sand adhere to the walls of the flask. The adherence to the walls is taken to indicate the presence of free liquid. The surface of the sand or beads is then determined, and the thickness of the film calculated. These experiments were carried out with water, nitrobenzene, aniline, dimethylaniline, iodobenzene, toluene, turpentine, and pyridine, and with sands and beads of varying diameter. The results show that there is no chemical combination between the liquid and the solid. The thickness of the film is independent of the liquid used and of the size of the solid particles. J. F. S.

Formulæ concerning Surface Tension. ARTHUR C. LUNN (*J. Amer. Chem. Soc.*, 1919, **41**, 620—621).—A theoretical discussion on the mathematical processes involved in the deduction of the formulæ used for calculating surface tension. J. F. S.

Determination of Surface Tension (Free Surface Energy), and the Weight of Falling Drops: Surface Tension of Water and Benzene by the Capillary Height Method.

WILLIAM D. HARKINS and F. E. BROWN (*J. Amer. Chem. Soc.*, 1919, **41**, 499—524).—The two methods in general use for the determination of surface tension are considered, the errors attached to each method are indicated, and a series of determinations of the surface tension of water and benzene are recorded. The theory of the capillary rise method is simple, but the technique is difficult, and its use in some cases causes errors as high as 30%, due to its inapplicability to certain classes of substances. The drop-weight method is applicable to a wide range of liquids, and the technique is not difficult; but the theory of this method has not been completely worked out, so that many of its published results are inaccurate, although the experimental data are accurate; this is due to the use of an inaccurate theory. The relation of the experimental results of the drop-weight method to those of the capillary rise method has been determined by using liquids which give accurate results by both methods, and this relationship has been plotted in such a way as to show the relation between surface tension and the form of the drop which falls from a circular tip. The surface tension and the capillary constant of water and benzene at 20°, each against air saturated with its own vapour, have been determined by the capillary rise method. The values obtained are: for water, $\gamma = 72.800$ dynes per cm., $a^2 = 14.897$ mm.; for benzene, $\gamma = 28.80$ dynes per cm., $a^2 = 6.713$ mm. In this determination, the capillary tubes were steamed out with the vapour of the liquid before use. In the case of water, this increased the value of γ by about 0.1 dyne. Water, benzene, carbon tetrachloride, and ethylene dibromide were dropped from a large number of glass and metal tips of radii varying from 0.09946 cm. to 1.0028 cm., and the weights of the falling drops determined. From the data, r/a and $f(r/a)$, of the Lohmstein equation,

$$Mg = 2\pi r \gamma f(r/a),$$

were calculated for values of r/a between 0.25 and 2.60. The value of $f(r/a)$ is not constant, but varies from 0.7256 to 0.5352 in this range, whilst when r/a falls to 0.025, $f(r/a)$ rises to 0.924. It is assumed that in conjunction with other necessary conditions, r/a really determines the shape of the hanging drop, and that it is the shape of the drop which determines the fraction of the drop which falls. This shape may also be determined by the ratio of r to the cube root of the volume of the falling drop. Thus a new equation, similar to that of Lohmstein, was derived,

$$Mg = 2\pi r \gamma \psi(r/v^{\frac{1}{3}}).$$

This is more easily applied to the determination of surface tension than Lohmstein's equation, since all the factors except γ are obtained by direct experiment or from a table of values, whilst the a of Lohmstein's equation cannot be obtained from the direct results of the drop-weight measurements, but must be calculated by methods of approximation.

J. F. S.

Osmotic-kinetic Theory of Dilute Solutions. G. JÄGER (*Zeitsch. physikal. Chem.*, 1919, **93**, 275—311).—A theoretical paper in which the relationship between pressure and volume of a highly compressed gas is deduced. It is shown both as a first approximation and also strictly that that portion of the pressure of a highly compressed gas occasioned by the arrangement of the molecules on a surface can be calculated as though no collisions between the molecules occurred. To this portion of the pressure there is to be added that occasioned by the collisions of the molecules. The sum of the two gives the pressure exerted on the walls of the containing vessel. Calculations show that for a solution an osmotic pressure is obtained which is the same as the value which would be obtained if the dissolved substance alone were present in the vessel. It is also shown that a dilute solution must have the same internal pressure as the pure solvent. The equations for the elevation of the boiling point and the lowering of the freezing point are developed from the vapour-pressure lowering. It is also shown that the Nernst theorem can be obtained from kinetic considerations, and that the relationship of the concentrations of a non-electrolyte in two sparingly soluble solvents is independent of the quantity of dissolved substance. J. F. S.

Rapid Determination of Solubility. T. J. WARD (*Analyst*, 1919, **44**, 137).—About 3 c.c. of the solvent are heated in a test-tube placed in a beaker of water about 10° to 20° higher than the temperature at which the solubility is to be determined, and small quantities of the substance are added, with constant shaking, until some remains undissolved. The test-tube is then immersed in water at the desired temperature for ten minutes, with occasional shaking, after which a thimble of filter-paper is pushed into the tube so that the liquid can filter inwardly. A definite volume of the filtrate is withdrawn by means of a pipette, weighed in a covered vessel, and evaporated, and the residue dried and weighed. C. A. M.

Coagulation of Metal Sulphide Hydrosols. I. Influence of Distance between the Particles of a Sol on its Stability. Anomalous Protective Action of Dissolved Hydrogen Sulphide. JÑANENDRA NATH MUKHERJEE and NAGENDRA NATH SEN (*T.*, 1919, **115**, 461—472).

The Chemical Equilibrium between Lead Sulphide and the Products of the Roasting Process. RUDOLF SCHENCK and AGNES ALBERS (*Zeitsch. anorg. Chem.*, 1919, **105**, 145—166).—The three-component system lead-sulphur-oxygen gives rise to seven solid phases, Pb, PbO, PbS, PbSO₄, PbSO₄.PbO, PbSO₄.2PbO, PbSO₄.3PbO, besides the gaseous phase SO₂. There are thirteen possible univariant systems, each consisting of three solid phases in equilibrium with the gaseous phase, and these

thirteen systems fall into three groups. In group I (4 systems), lead sulphide is in equilibrium with two oxygen-containing phases; in group II (5 systems), lead sulphide and metallic lead are in equilibrium with one oxygen-containing phase; and in group III (4 systems), metallic lead with two oxygen-containing phases. The vapour-tension curves for the systems of groups I and II have been investigated at temperatures between 500° and 820° . Earlier measurements of the vapour tensions of some of these systems were made by Schenck (A., 1907, ii, 546, 619) and Reinders (A., 1915, ii, 47), but their results were to some extent vitiated through the use of silica vessels, which were attacked by the reaction mixtures. This difficulty has been overcome by the use of calcium phosphate for the containers. The pressure-temperature diagram for the nine systems investigated is given. The most stable phases are those of group II, in which both lead and lead sulphide are present as solid phases, these systems being in equilibrium with a lower pressure of sulphur dioxide than those of group I. The vapour phase always contains lead sulphide. It follows that in the systems of group III, in which lead sulphide is not present as a solid phase, the vapour must be unsaturated with respect to lead sulphide. A complete equilibrium diagram, including the systems of group III, must therefore be in three dimensions, the third co-ordinate representing the vapour pressure of lead sulphide. It was found impossible to realise experimentally the conditions of existence of the systems of group III, as they are apparently very unstable.

The vapour pressure of lead sulphide between 850° and 1000° was measured, and was found to increase from 2 mm. to 17 mm. between these temperatures. Lead sulphide distils readily in a vacuum at 900° .
E. H. R.

The Action of Salts. K. SPIRO (*Biochem. Zeitsch.*, 1919, **93**, 384—394).—Many ions may have an influence on quite simple chemical reactions in which they are apparently not directly concerned. The influence of the ions may be arranged in order of magnitude, resembling the Hofmeister series.

The reactions studied included the oxidation of potassium iodide by atmospheric oxygen and hydrogen peroxide, the oxidation of indigo, the guaiacum reaction, the reducing action of hydrogen peroxide on ferric chloride and potassium ferricyanide, the oxidation of ammoniacal cuprous and silver oxides by dextrose, the indophenol reaction, and the action of catalase. The series of ions are not identical in every case. The presence of magnesium may in certain cases exert a more favourable action on oxidation processes than that of sodium, but examples of the reverse condition occur. Certain examples of the influence of foreign ions may be considered to be analogous to co-enzyme actions. It is apparent, however, that the lyotropic series may apply for simple chemical reactions as much as for physico-chemical reactions, such as imbibition or emulsification.
J. C. D.

Catalytic Action of Hydrogen Ions in Hydrolyses. RUD. WEGSCHEIDER (*Ber.*, 1919, **52**, 235—236).—The failure of hydrogen ions to catalyse the hydrolysis of β -lactones is not the first example of abnormality in hydrion catalysis (see Johansson and Sebelius, A., 1918, ii, 223). Sulphonic esters are also known to be uninfluenced in this way, although the hydrolysis of alkyl hydrogen sulphates is catalysed by hydrions. J. C. W.

Temperature-coefficient of Catalysed and Non-catalysed Reactions. N. R. DHAR (*Ann. Chim.*, 1919, [ix], **11**, 130—223).—A more detailed account of work already published (T., 1917, **111**, 707). W. G.

Conception of Chemical Elements and Atomic Weight Tables. RUD. WEGSCHEIDER (*Zeitsch. physikal. Chem.*, 1919, **93**, 380—381).—Polemical against the definition of the term element put forward by Paneth (compare A., 1916, ii, 240; 1918, ii, 304). J. F. S.

Valency Theory. A. E. LACOMBLÉ (*Zeitsch. physikal. Chem.*, 1919, **93**, 257—274).—A theoretical paper in which, on the basis of Kossel's (A., 1916, ii, 243) conception of the atom, the author develops a theory of valency. As hypothesis, the following assumptions are made: (i) The electrons situated on the outside ring are stationary. (ii) A sphere is supposed to surround the atom in such a way that its centre lies at the centre of gravity of the atom, and only the outermost sheath falls outside the atom. The field of forces of the nucleus is regarded as that of a sphere of stated size having on its surface an irreplaceable positive charge of dimensions equal to, but opposite in sign to, the sum of the electrons on the outermost sheath. (iii) Chemical combination is regarded as the replacement of the curved lines of force between atoms and their electrons by shorter and straight lines of force. On the basis of these assumptions, the nature of the compounds which are formed between various elements is deduced. For example, it follows that the stability of the oxygen derivatives of the halogens increases with increasing atomic weight of the halogen. The halogen derivatives of the elements of group 6 increase in stability with increasing atomic weight of the element of the sixth group. Many other cases are developed. The nature of the bonds in the formation of molecules of elements is considered. This is divided into three types, which differ in the density of the lines of force on the atoms. The paper concludes with a description of the nature of the bonds of organic compounds. J. F. S.

The Mythical Basil Valentine. W. HOMMEL (*Zeitsch. angew. Chem.*, 1919, **32**, i, 73—76).—Although the existence of the alleged fifteenth-century monk, Basil Valentine, was doubted by Gmelin (1797), and by Kopp in his later work (1886), he is still, in many quarters, regarded as the last of the alchemists.

Anachronisms in the supposed writings of Basil Valentine prove that these could not have been written as early as 1460. All the evidence indicates that the name was a pseudonym for Johann Thölde, who, in 1603—1604, first published the writings of "Basil Valentine." The survival of the myth down to the present day is largely attributable to the account in Kopp's "Geschichte der Chemie" (1843), whilst Kopp's later conclusion on the subject has been overlooked.

C. A. M.

Simple Efficient Vacuum Pump for Laboratories. MAX VOLMER (*Ber.*, 1919, 52, [B], 804—809).—The pump is constructed on principles similar to those of Langmuir (*Phys. Rev.*, 1916, 8, 48) and Kraus (*A.*, 1917, ii, 567), from which it differs considerably in detail. The mercury is boiled in a glass vessel, and the vapour, passing through a narrow tube into the cooling chamber, carries with it the air from the vessel to be exhausted and passes it into the fore-vacuum of a water pump; the condensed mercury flows back by a side-tube to the bottom of the boiler, direct connexion between the fore- and main-vacua being prevented by a bent tube, in which mercury collects. The apparatus is figured in the original.

The average efficiency of the pump is such that a litre flask can be exhausted from 15 mm. to $<1/100$ mm. in five minutes, but differs somewhat with different individuals, as it depends on small factors which cannot invariably be reproduced. It is easily manipulated and cleaned. Vapours are removed as readily as gases, and it is not sensitive to moderate amounts of halogens. Its use is recommended for drying substances and for distillation under greatly diminished pressure. By the aid of the pump, more complete desiccation can be effected in thirty minutes than by exposure to alkali hydroxide at 10 mm. during twenty-four hours.

H. W.

Gas Washing Flask, especially for Use in the Estimation of Sulphur Dioxide in Flue Gases. H. SCHILLING (*Chem. Zeit.*, 1919, 43, 167).—The central inlet tube and the exit tube leading from the stopper of the flask are connected by means of a short length of tube provided with a tap. By means of the latter, when suitably turned, the gases may be directed through the solution contained in the flask or passed directly through the connecting tube and tap without entering the flask.

W. P. S.

Very Simple Form of Electrolytic Current Interrupter for Demonstration Purposes. KARL BRUNNER (*Ber.*, 1919, 52, [B], 629—630).—The apparatus consists of a glass trough with parallel sides, holding about 2 litres; on the one side, a lead plate, 9×13 cm., is suspended in 8% sulphuric acid. A board, laid on the top of the vessel, serves as adjustable support for a glass tube of 16 mm. diameter, at the bottom of which a hole, 3—4 mm. in diameter, is blown. The hole is partly closed by a pointed glass

rod, 50 mm. long and weighing 0.9 gram, which forms a valve opening in the upward direction. A strip of lead, 10 mm. wide, extends to the bottom of the tube. The apparatus is readily constructed from available material. In comparison with the Wehnelt interrupter, it gives a rather shorter spark, but is more trustworthy and less noisy in action.

H. W.

Lecture Experiment [Combustion of Phosphorus]. KARL BRUNNER (*Ber.*, 1919, **52**, [B], 631—632).—The phenomena attending the combustion of phosphorus are conveniently and safely demonstrated in the following manner. The apparatus consists of two doubly tubulated glass vessels holding about a litre, which are connected by a short length of slightly bent quartz tube; the other tubulures carry a mercury manometer and a stopcock respectively. About 0.5 gram of yellow phosphorus is placed in the quartz tube, and the complete apparatus is accurately counterpoised. The phosphorus is ignited by gently warming the tube, and slow combustion is maintained by occasional gentle warming of the glass vessels. When combustion is complete, the apparatus is left to itself until the manometer indicates a deficiency in internal pressure. The weight is found to be unaltered. The stopcock is now opened, when a distinct increase in weight is caused by the intruding air.

H. W.

Preparation of Phosphorus Trioxide as a Lecture Experiment. HEINRICH BILTZ and ANNA GROSS (*Ber.*, 1919, **52**, [B], 762—768).—The apparatus consists of a combustion tube, 30 cm. long and 1.8—2.0 cm. internal diameter, which is drawn out to a point and turned upwards at one end. This is connected with a filter tube, 25 cm. in length and of the same diameter as the first tube, which contains a loose plug of cotton wool and a layer of 6 cm. of tightly compressed cotton-wool balls. During the experiment, the tube (which is preferably made of brass) is heated at 50—60° by a small flame. A condensation tube, 75 cm. long and 2 cm. wide, is connected with the filter tube and, through a wash-bottle containing sulphuric acid, to a filter pump. About 10 grams of phosphorus are placed in the combustion tube, the filter tube is warmed, and the experiment started by gently warming the phosphorus until it is just ignited; after about two minutes, when the tube has become warmed, the speed of the air stream is considerably increased. After five to ten minutes, phosphorus trioxide begins to appear in the condensation tube, which is cooled, if necessary, by a cloth dipped in ice-water. The experiment must be stopped before the phosphorus is completely burnt; if not, oxygen gets access to the phosphorus trioxide and causes oxidation. The crystalline nature and low m. p. of the trioxide are readily demonstrated; the oxidisability is shown by opening the tube in the dark, when a luminescence is shown which develops into active combustion when the tube is warmed or by dissolving the substance

in carbon disulphide, so as to obtain a dilute solution, which is then poured on to filter paper.

The authors are led to the conclusion that phosphorus trioxide is always the primary product of the combustion of phosphorus, and that formation of the pentoxide is a subsequent reaction. They therefore recommend the use of a rapid air current, since this ensures on the one hand a rapid combustion, and consequent complete removal of oxygen from the residual gases, and on the other a rapid withdrawal and cooling of the phosphorus trioxide, which is otherwise readily decomposed into phosphorus pentoxide and red products.

The yield of phosphorus trioxide is only moderate, and the addition of indifferent gases, either before or behind the zone of combustion, does not effect sufficient improvement to justify the complication involved.

H. W.

Inorganic Chemistry.

Hypochlorous Acid and Chlorine Monoxide. STEFAN GOLDSCHMIDT (*Ber.*, 1919, **52**, [B], 753—761).—Aqueous solutions of hypochlorous acid containing 25% of the acid are readily obtained by distilling a mixture of chlorine hydrate and yellow mercuric oxide in a good vacuum; attempts to prepare the more concentrated solution or the anhydrous acid by distillation of this acid in a moderate vacuum, and condensation of the distillate in receivers maintained at 0°, -20°, and -80°, led to an unexpected result, since in the first two vessels aqueous hypochlorous acid (25%) was collected, whilst in the third vessel pure chlorine monoxide was condensed (the pure monoxide has b. p. +3·8°/766 mm. and can only be preserved without decomposition for any length of time at -80°). It therefore appeared that the aqueous acid contains two systems in equilibrium: (1) $\text{HClO} \rightleftharpoons \overset{+}{\text{H}} + \overset{-}{\text{OCl}}$, and (2) $\text{HClO} \rightleftharpoons \text{Cl}_2\text{O} + \text{H}_2\text{O}$. The latter system has been investigated by agitating aqueous hypochlorous acid solutions of different concentration with an equal volume of carbon tetrachloride at 0°, separating the solutions, and estimating the active chlorine in each by titration with sodium thiosulphate after treatment with acidified potassium iodide solution. The equilibrium lies greatly in favour of the hypochlorous acid, so that an approximately *N*/5-solution contains 0·02% of the anhydride.

The well-known greater oxidising power of hypochlorites in acid than in alkaline solution is probably due to chlorine monoxide contained in the former solutions.

H. W.

Preparation of Sulphuryl Chloride. A. BOAKE ROBERTS AND Co., LTD., and THOMAS HAROLD DURRANS (Brit. Pat., 124542).—Sulphur dioxide and chlorine, in equal volumes, are passed either together or alternately, and either continuously or intermittently, into a vessel containing a suitable catalyst. The temperature must be kept sufficiently low to prevent the catalyst and the sulphuryl chloride formed from volatilising, and sufficiently high to prevent the catalyst from solidifying. The sulphuryl chloride may be isolated by distillation or other suitable means.

The following classes of substance are effective as catalysts, and do not require the aid of light or pressure, the most suitable members of each class being placed within brackets: terpene hydrocarbons (pinene and limonene); esters which are compounds of saturated acids or of monohydroxyphenols with monobasic aliphatic acids containing carbon, hydrogen, and oxygen only (methyl acetate, *iso*amyl formate, ethyl butyrate, phenyl acetate, phenylethyl acetate, glyceryl triacetate, oils which are esters of glycerol, and also triphenyl phosphate and tritolyl phosphate); ethers which are the mixed or simple saturated aliphatic ethers (ethyl ether, *isobutyl* ether, benzyl ether, tolyl ether), and the terpene ether, cineole (eucalyptol); the saturated monohydroxyphenols which contain only one benzene ring. The ethers, phenols, and esters are limited to those which contain carbon, hydrogen, and oxygen only, and no substituting groups except those containing only carbon and hydrogen. [See also *J. Soc. Chem. Ind.*, 1919, June.]

H. W.

Colloidal Selenium. JULIUS MEYER (*Zeitsch. Elektrochem.*, 1919, **25**, 80—82).—Colloidal selenium may be obtained by the action of dilute sulphuric acid on sodium selenosulphate according to the equation $\text{Na}_2\text{SeSO}_3 + \text{H}_2\text{SO}_4 = \text{Se} + \text{SO}_2 + \text{H}_2\text{O} + \text{Na}_2\text{SO}_4$. A small quantity of sodium sulphite is dissolved in 5 c.c. of distilled water and boiled with an equal quantity of selenium for about half a minute, the solution is filtered, and about 1 c.c. of the filtrate diluted with a litre of water, treated with four to five drops of dilute sulphuric acid, and stirred. The solution becomes at once orange-yellow to dark red in colour, depending on the concentration. Filtration through a Zsigmondy membrane gives a clear, colourless sol. The sols are very stable and not at all sensitive to moderate concentrations of acids. The particles are positively charged, and thus differ from the colloidal selenium produced by the solution of selenium in hydrazine hydrate, which is negatively charged. A comparison of the two forms of colloidal selenium is given in the paper, and the suitability of the new form for lecture experiments is demonstrated.

J. F. S.

The Decomposition of Nitrous Acid. JOSEPH KNOX and DOUGLAS M. REID (*J. Soc. Chem. Ind.*, 1919, **38**, 105—108T).—The nitrous acid solutions for these experiments were prepared by mixing solutions of nitric acid and sodium nitrite of known

strengths. The rate of decomposition of the nitrous acid was found to be profoundly influenced by the conditions. It is greatly accelerated when the amount of surface exposed to the action of air is increased, for example, by shaking in presence of excess of air. The excess of air is effective through removing by oxidation the nitric oxide produced in the reversible reaction, $3\text{HNO}_2 \rightleftharpoons \text{HNO}_3 + 2\text{NO} + \text{H}_2\text{O}$, thus allowing the balanced reaction to proceed in the direction from left to right. The nitric oxide can also be removed from the solution by the passage of a current of carbon dioxide, the decomposition being accelerated almost as much as by a current of air. The influence of temperature on the rate of decomposition with, and without, excess of air was studied up to 50° , and the rate was found to increase rapidly with the temperature. Free nitric acid, if present, accelerates the initial rate of decomposition of the nitrous acid, but appears to have a retarding influence in the later stages. The several series of experiments are illustrated by curves. E. H. R.

Densities of Mixtures of Sulphuric and Nitric Acids. PAUL PASCAL and M. GARNIER (*Bull. Soc. chim.*, 1919, [iv], **25**, 142—145).—Tables are given showing the results of determinations of the density of sulphuric and nitric acids at different concentrations, and of mixtures of these acids in varying proportions and with varying proportions of water added. It is shown that, in the zone of mixtures used for nitrating cotton, the density is almost entirely a function of the water content. W. G.

Baeyer's Strain Theory and the Structure of the Diamond. ERNST MOHR (*J. pr. Chem.*, 1918, [ii], **98**, 315—353).—A theoretical paper in which the stability of the *cyclohexane* ring is first considered; it is shown that the number of known isomerides is readily explicable by means of Lachse's model (in which the carbon atoms do not lie in one plane) if, at the same time, a free or only partly hindered rotation is assumed. The ideas are extended to more complex rings, but the data are too restricted to allow any very general conclusions to be drawn.

It is further shown that atom model systems can be constructed by the direct or oblique superposition of *cyclohexane* ring layers in the centre of which all valencies are saturated without strain and in which free valencies exist only at the surface. The diamond space lattice described by Bragg is then found to be identical with the obliquely formed carbon atom system so derived.

The existence of carbon rings which contain more than six carbon atoms and which are free from strain is also considered, but the author is led to the conclusion that the strain in such systems cannot at present be predicted with any certainty, and is probably complicated by other factors. H. W.

Attempted Synthesis of Carbonyl Sulphide by means of the Electric Spark. F. GONZÁLEZ and E. MOLES (*Anal. Fis. Quím.*, 1919, **17**, 55—59).—The assertion of Chevrier (*Compt.*

rend., 1869, **69**, 136) that sulphur vapour and carbon monoxide combine easily under the action of the electric spark to form carbonyl sulphide was tested by the authors. Pure dry carbon monoxide was passed in a sealed apparatus over the surface of sulphur heated at 110° and 260°, and there subjected to sparking. The gaseous products were cooled in various freezing mixtures, finally in liquid air. No trace of carbonyl sulphide was observed. An experiment under reduced pressure also yielded a negative result.

W. S. M.

Thermal Decomposition of Carbonyl Sulphide. ALFRED STOCK and PAUL SEELIG (*Ber.*, 1919, **52**, [B], 681—694).—The thermal decomposition of carbonyl sulphide leads to the formation of carbon monoxide and sulphur on the one hand and to carbon dioxide and carbon disulphide on the other; assuming that carbon oxysulphide is immediately concerned with each equilibrium, the reactions may be written $2\text{COS} \rightleftharpoons 2\text{CO} + \text{S}_2$ and $2\text{COS} \rightleftharpoons \text{CO}_2 + \text{CS}_2$. Attempts have now been made to determine the equilibrium at 800° and 950° respectively. For this purpose, a current of carbonyl sulphide is sent through an electrically heated quartz tube packed with quartz splinters and provided with a quartz rod to prevent backward diffusion of gas; the end of the quartz tube is drawn out to a capillary connected as closely to the furnace as possible with a quartz U-tube, which is immersed in a paraffin bath maintained at 130°, and serves to retain the sulphur; the gases evolved are collected over mercury and analysed by the authors' method (this vol., ii, 245). The effect of the rate of passage of gas (time of heating) and rapidity of cooling (length of capillary) has been investigated, from which it appears that the values observed approximate closely to the true equilibria values.

At 800°, the reaction $2\text{COS} \rightleftharpoons \text{CO}_2 + \text{CS}_2$ appears to proceed slowly in either direction, whilst the action $2\text{COS} \rightleftharpoons 2\text{CO} + \text{S}_2$ is very rapid. The fact that the carbon monoxide degree of dissociation is independent of the amounts of carbon dioxide and carbon disulphide present shows that carbon monoxide and sulphur (at any rate for the greater part) are primary products of the decomposition of carbonyl sulphide, and not formed secondarily from carbon dioxide and carbon disulphide. The CO_2 degree of dissociation is about 48·5%, the CO degree about 45·5%, so that, at 800° and atmospheric pressure, the carbonyl sulphide is decomposed to the extent of about 64%. At 950°, the corresponding figures are 43% for the CO_2 degree of dissociation, at least 71% for the CO degree, and at least 76% for the dissociation of carbon oxysulphide.

[With W. OTTMANN.]—Preliminary experiments on the action of heat on mixtures of carbon dioxide and disulphide on the one hand and of carbon monoxide and sulphur on the other show that the same products are formed as when carbonyl sulphide is heated, and that a true case of equilibrium is presented. Similarly, the combustion of carbon disulphide with an insufficiency of oxygen

or of oxygen in carbon disulphide vapour yields a mixture of unchanged carbon disulphide, carbon dioxide, sulphur dioxide, carbonyl sulphide, and carbon monoxide.

The literature of the subject is also critically reviewed.

H. W.

Stabilisation of Dilute Sodium Hypochlorite Solutions (Dakin's Solution). GLENN E. CULLEN and ROGER S. HUBBARD (*J. Biol. Chem.*, 1919, **37**, 511—517).—The regulation of the alkalinity of Dakin's solution may be efficiently carried out either by means of buffer salts or by small amounts of alkali. 0.5% Sodium hypochlorite, prepared by electrolysis of sodium chloride, may be stabilised for use by the addition of 0.5% borax, of 0.5 to 1.0% of sodium carbonate mixtures of p_H 10 to 9.5, or by the addition of 0.2 gram of sodium hydroxide per litre. J. C. D.

Electrolytic Preparation of Dilute Sodium Hypochlorite Solutions (Dakin's Solution). GLENN E. CULLEN and ROGER S. HUBBARD (*J. Biol. Chem.*, 1919, **37**, 519—523).—The influence of temperature on this process was investigated. The optimum point of the curve representing the production of hypochlorite may be raised by raising the initial temperature of the brine. Increase of salt concentration lessens the internal resistance of the cell, and consequently increases the production of sodium hypochlorite per unit of time. [See, further, *J. Soc. Chem. Ind.*, 1919, June.]

J. C. D.

The Stability of Javel Extracts. H. FONZES-DIACON (*Bull. Soc. chim.*, 1919, [iv], **25**, 206—208).—Javel extracts, containing 5 grams of active chlorine per 100 c.c., lose very little of their activity when exposed to light in deep yellow bottles, even after four months. In colourless bottles, the loss is very marked, however, Javel extracts of various strengths tending towards a common limit of about 1 gram of active chlorine per 100 c.c. W. G.

Chemical Decomposition and Electrolytic Formation of Sodium Hyposulphite. K. JELLINEK and E. JELLINEK (*Zeitsch. physikal. Chem.*, 1919, **93**, 325—367).—The decomposition of sodium hyposulphite has been studied in aqueous solution and in solutions of sodium hydrogen sulphite of various concentrations at the temperatures 0°, 10°, 20°, and 30°. The reaction follows the scheme $2Na_2S_2O_4 = Na_2S_2O_5 + Na_2S_2O_3$; $Na_2S_2O_5 + H_2O = 2NaHSO_3$. The reaction is bimolecular, and the constants have been obtained for the various temperatures. The dependence of the reaction constant on temperature and on the hydrogen sulphite concentration is given by the equation $\log k = A + Bt$, in which A and B are constants. At constant temperature, the reaction constant is proportional to the square of the hydrogen sulphite concentration. The electrolysis of sodium hyposulphite has been investigated, particularly in connexion with the factors which

govern the hyposulphite formation. The electrolysis was carried out with electrodes of various metals, and variable quantities of sulphur dioxide were led into the solution. The concentration of sodium thiosulphate and the amount of hydrogen liberated were measured, and the dependence of these on the time of electrolysis determined. Solutions containing 7—8% of hyposulphite could be obtained. The processes which influenced the current yield were quantitatively explained, and the conditions for obtaining higher yields of hyposulphite indicated.

J. F. S.

Cryoscopic Study of Couples. Cadmium Iodide-Alkali Iodide. E. CORNEC and G. URBAIN (*Bull. Soc. chim.*, 1919, [iv], 25, 137—142).—For the most part a more detailed account of work already published (compare A., 1914, ii, 428). A cryoscopic study of the couple cadmium iodide-hydrogen iodide in aqueous solution reveals the existence in aqueous solution of the acid salt, $\text{CdI}_2 \cdot 2\text{HI}$.

W. G.

The Preparation of Cadmium Suboxide. HENRY GEORGE DENHAM (*T.*, 1919, 115, 556—559).

New Preparation of a very Dissociable Calomel. PAUL DURET (*Ann. Inst. Pasteur*, 1919, 33, 174—176).—Calomel may be prepared in a light, voluminous form having a high degree of purity by the following process. A solution containing 6 grams of sodium hydrogen carbonate and 10 grams of dextrose in 80 c.c. of water is added to a solution containing 7.5 grams of crystalline magnesium chloride in 20 c.c. of water, and this mixture is added to a solution containing 11.5 grams of mercuric chloride and ten drops of hydrochloric acid in 100 c.c. of water in a flask. When the reaction has ceased, the mixture is heated on a water-bath until all the carbon dioxide is evolved. The finely divided precipitate of mercurous chloride is then collected and washed with water. In this form it possesses greater germicidal powers than the ordinary preparations when used in prophylactic ointments or anti-syphilitic injections.

W. G.

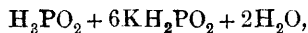
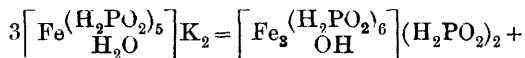
Regeneration of Nessler's Solution. D. PULLMAN (*Analyst*, 1919, 44, 124—125).—Residues from the estimation of ammonia by Nessler's method are neutralised and treated with a solution of a soluble mercuric salt in amount equivalent to the iodine present. This precipitates mercuric iodide, which may be washed, dried, and used for the preparation of a modified Nessler's solution. This is made by adding metallic zinc to mercuric iodide suspended in hot water, when the reaction, $\text{Zn} + 2\text{HgI}_2 = \text{ZnHgI}_4 + \text{Hg}$, takes place. The zinc mercuric iodide remains in solution, and, after filtration from the mercury, is treated with sodium hydroxide in sufficient quantity to produce the reagent. Experiments have shown that Nessler's reagent thus prepared can replace the ordinary solution containing potassium mercuric iodide. [See also *J. Soc. Chem. Ind.*, 1919, June.]

C. A. M.

Mercuric Sulphoxychloride. SIR PRAFULLA CHANDRA RÂY and PRAFULLA KUMAR SEN (T., 1919, 115, 552—556).

Manganates and Permanganates. I. Course of the Reaction between Manganese Dioxide, Potassium Hydroxide, and Oxygen, and the Manufacture of Potassium Manganate. H. I. SCHLESINGER, R. D. MULLINIX, and S. POPOFF (*J. Ind. Eng. Chem.*, 1919, 11, 317—323).—When manganese dioxide is heated with potassium hydroxide in a current of air, complete oxidation is frequently attained only by re-moistening and re-heating the mixture. The yield of potassium manganate varies with the proportion of potassium hydroxide present; at about 300°, practically all the manganese dioxide is converted into manganate when two molecules of potassium hydroxide are used for each molecule of manganese dioxide. Mangani-manganates are not formed under these conditions, but larger amounts of potassium hydroxide cause the manganate to decompose into mangani-manganate (compare Sackur, A., 1911, ii, 400). The yield of manganate is lowered when sodium hydroxide is used in place of potassium hydroxide. It is important that the manganese ores used should be powdered as finely as possible. [See, further, *J. Soc. Chem. Ind.*, 1919, 321A.] W. P. S.

Complex Compounds of Tervalent Iron with Hypophosphorous Acid. R. F. WEINLAND and WALTER HIEBER (*Ber.*, 1919, 52, [B], 731—741).—In a previous communication (*Zeit. anorg. Chem.*, 1919, 106) it has been shown that tervalent iron forms a complex cation with hypophosphorous acid, $[\text{Fe}_3(\text{H}_2\text{PO}_2)_6]^{+++}$. It is now established that a similar complex anion can also exist. If the basic ferric hypophosphite, $\text{Fe}_3(\text{H}_2\text{PO}_2)_8\cdot\text{OH}$, is dissolved in warm concentrated solutions of alkali hypophosphites and the solutions are allowed to evaporate, pale reddish-violet crystals separate having the composition $\text{Fe}(\text{H}_2\text{PO}_2)_3\cdot 2\text{K}(\text{Na})\text{H}_2\text{PO}_2\cdot\text{H}_2\text{O}$. The molecule of water is firmly retained. The properties of these salts lead the authors to ascribe to them the constitution $[\text{Fe}(\frac{\text{H}_2\text{PO}_2}{\text{H}_2\text{O}})_5] \text{K}_2(\text{Na}_2)$. When the salts are dissolved in water, a basic ferric hypophosphite is precipitated,



a complex cation being thus transformed into a complex anion; the latter is only stable in solution in the presence of a large excess of alkali hypophosphite, and the composition of the basic salt varies somewhat.

Since hypophosphorous acid and ferric iron can thus combine to form both complex acid and complex base, it is to be expected that these will combine with one another to yield salts which appear to be ferric hypophosphites. Their constitution follows from their mode of formation. Thus, if concentrated ferric chloride solution

is slowly added to warm concentrated alkali hypophosphite, the ferric hypophosphite formed is immediately dissolved, yielding the complex pentahypophosphito-ion; on continued addition, however, a sudden precipitation occurs, and further precipitations can be obtained from the successive filtrates. These salts are all feebly basic or practically neutral, the composition of which varies between $\text{Fe}:\text{H}_2\text{PO}_2=1:2.71$ and $1:2.86$. *Salts* are thus obtained containing (i) two hexahypophosphito-cations, one pentahypophosphito-anion, and two hypophosphite radicles; (ii) a similar salt containing three hypophosphite radicles, and (iii) a salt composed of one complex anion and cation. Similarly, when a solution of ferric hypophosphite in hypophosphorous acid (50%) is evaporated over sulphuric acid, a salt is obtained containing one triferrihexahypophosphito-cation and one pentahypophosphito-anion, and either three or four molecules of hypophosphorous acid.

The ability of hypophosphorous acid to yield both complex anions and cations with ferric iron is shared only by formic and salicylic acids; the reason may possibly lie in the somewhat similar structure, $\text{H}\cdot\text{C}\begin{smallmatrix} \text{O} \\ \text{OH} \end{smallmatrix}$ and $\text{H}_2\cdot\text{P}\begin{smallmatrix} \text{O} \\ \text{OH} \end{smallmatrix}$, of formic and hypophosphorous acids.

H. W.

The Normal Nitrides of Nickel and Cobalt. A. C. VOURNASOS (*Compt. rend.*, 1919, **168**, 889—891).—*Nickel nitride*, Ni_3N_2 , is readily obtained if a mixture of anhydrous nickelous oxide and anhydrous nickel cyanide in the proportion of 1:0.74 is dropped in small quantities at a time through an arc between two carbon electrodes in an atmosphere of nitrogen, providing the temperature of the arc is near 2000° . The nitride so obtained is not magnetic. It burns in oxygen, giving nickelous oxide and nitrogen peroxide. It is decomposed when heated in chlorine, and also by nitric and hydrochloric acids. It is not decomposed by boiling water.

Cobalt nitride, Co_3N_2 , a brown powder, may be similarly prepared, and possesses similar properties.

W. G.

Existence of isoTungstic Acid. P. BARBE (*Mon. Sci.*, 1919, [v], **9**, i, 73—75).—Results of a critical research led the author to the opinion that isotungstic acid and ammonium isotungstate do not exist; the ammonium isotungstate described by Gerber (A., 1917, ii, 575) was actually ammonium sodium tungstate. The author has worked for some years on tungsten, and, without going as far as to deny the existence of neotungsten, states that he has never met with a specimen of the metal having a molecular weight higher than usual. [See, further, *J. Soc. Chem. Ind.*, 1919, June.]

W. P. S.

Mineralogical Chemistry.

Oruetite, a New Sulphotelluride of Bismuth. S. PIÑA DE RUBIES (*Anal. Fis. Quím.*, 1919, 17, 83—87).—This mineral, discovered in the Serranía de Ronda, in Spain, occurs on dolomite in laminar masses accompanied by scheelite, pyrites, mispickel, limonite, bismuthite, and native bismuth. The laminæ show a brilliant steel-grey, metallic lustre, and are easily exfoliable. Hardness, 1·5—2. Density, 7·6. The resemblance to tetradymite is very marked. The mean of seven analyses gave: Bi 86·78%, Te 6·35%, S 6·84%. This analysis is in agreement with the formula Bi_8TeS_4 . A study of the ternary system bismuth—sulphur—tellurium shows the existence of the compounds Bi_2S_3 , Bi_2Te_3 , and $\text{Bi}_2\text{Te}_3\cdot\text{Bi}_2\text{S}_3$ (Amadori, A., 1918, ii, 366), the naturally occurring sulphotellurides, tetradymite (variety with sulphur), joseite, grünlite, oruetite, being regarded as eutectic mixtures. The author proposes the following representation of these eutectics: tetradymite (with sulphur), $\text{Bi}_2\text{Te}_3\cdot\text{Bi}_2\text{S}_3$ — Bi_2Te_3 ; joseite, $\text{Bi}_2\text{Te}_3\cdot\text{Bi}_2\text{S}_3$ — $5\text{Bi}?$; grünlite, $\text{Bi}_2\text{Te}_3\cdot\text{Bi}_2\text{S}_3$ — $2\text{Bi}_2\text{S}_3$ — 4Bi ; oruetite, $\text{Bi}_2\text{Te}_3\cdot\text{Bi}_2\text{S}_3$ — $3\text{Bi}_2\text{S}_3$ — 14Bi .

W. S. M.

Hydrated Ferric Oxides. EUGEN POSNJAK and H. E. MERWIN (*Amer. J. Sci.*, 1919, [iv], 47, 311—348).—Analyses of a number of naturally occurring hydrated ferric oxides, from many localities, have been made, and the detailed results given in the paper. Dehydration curves and specific gravities of some of the specimens have been obtained. The experiments show that there is only one hydrate of natural ferric oxide, and this is the monohydrate. The descriptions given in the literature of a series of hydrates ranging from $\text{Fe}_2\text{O}_3\cdot\frac{1}{2}\text{H}_2\text{O}$ to $\text{Fe}_2\text{O}_3\cdot 3\text{H}_2\text{O}$ are therefore erroneous. The monohydrate occurs in nature in two polymorphic forms, goethite and lepidocrocite, and in an amorphous condition, limonite. *Goethite* is orthorhombic, $a:b:c=0\cdot91:1:0\cdot602$, $D\ 4\cdot28\pm0\cdot01$, $\alpha\ 2\cdot26$, $\beta\ 2\cdot394$, $\gamma\ 2\cdot400$; it has a dull orange-yellow streak and a faint pleochroism. *Lepidocrocite* is orthorhombic, $a:b:c=0\cdot43:1:0\cdot64$, $D\ 4\cdot09\pm0\cdot04$, $\alpha\ 1\cdot94$, $\beta\ 2\cdot20$, $\gamma\ 2\cdot51$; it has a dull orange streak and a very strong pleochroism. *Limonite* is essentially isotropic ferric oxide monohydrate with adsorbed and capillary water. The fibrous mineral *turgite* is variable in composition, and is probably a solid solution of goethite in hæmatite with enclosed and adsorbed water. No definitely crystallised synthetic hydrated ferric oxide has been prepared, and only two types of amorphous hydrated ferric oxide exist, one yellow and the other reddish-brown. The yellow substance is essentially ferric oxide monohydrate, whilst the reddish-brown substance may hold its water either in a dissolved or an absorbed condition, or both.

J. F. S.

Turite (= Turgite) and other Iron-Ores from Nova Scotia.

L. J. SPENCER (*Min. Mag.*, 1919, **18**, 339—348).—The group of ferric hydroxide minerals include the following species (hæmatite being added to complete the series):

		H ₂ O%.	Sp. gr.
Hæmatite.....	Fe ₂ O ₃	0·0	5·2
Turite	2Fe ₂ O ₃ ·H ₂ O	5·3	4·3
Goethite	Fe ₂ O ₃ ·H ₂ O	10·1	4·2
Hydrogoethite ...	3Fe ₂ O ₃ ·4H ₂ O	13·1	3·7
Limonite	2Fe ₂ O ₃ ·3H ₂ O	14·5	3·9
Xanthosiderite ...	Fe ₂ O ₃ ·2H ₂ O	18·4	—
Limnite	Fe ₂ O ₃ ·3H ₂ O	25·3	2·8
Esmeraldaite	Fe ₂ O ₃ ·4H ₂ O	31·1	2·6

Of these, goethite is the only one that occurs as distinct crystals; the remainder have sometimes been regarded as colloids of indefinite composition, and in some of the recent text-books are treated all together under limonite. Turite and limonite possess, however, a fibrous, crystalline structure with definite optical characters, and their dehydration curves are quite distinct from one another and from that of goethite. Turite (the more familiar spelling, turgite, is an incorrect German transliteration from the Russian) usually occurs as a layer on limonite, and forms hard ($H = 6\frac{1}{2}$), lustrous, mamillated or botryoidal masses with a radially-fibrous and concentric-shelly structure. It is black with often a reddish tinge of colour and a brilliant sub-metallic lustre; the streak is dark cherry-red, and very thin fibres transmit a crimson colour. It decrepitates violently when heated.

The other Nova Scotian iron ores include magnetite, hæmatite, chalybite, mesitite, ankerite, and brilliant pseudomorphous crystals of hæmatite after goethite.

L. J. S.

The Occurrence of Polyhalite in the Older Zechstein Potassium Salt Deposits in Relation to Van't Hoff's Conclusions.

M. ROSZA (*Zeitsch. anorg. Chem.*, 1919, **105**, 167—170).—The occurrence of primary and secondary deposits of polyhalite, Ca₂K₂Mg(SO₄)₄·2H₂O, is in general agreement with what is to be expected from van't Hoff's work. The salt is met with in almost all potassium-containing parts of the older Zechstein salt deposits, with the exception of the carnallite layers. As a primary deposit, it is found here and there in the "Steinsalz." Elsewhere, as in the kieserite transition zone of the Stassfurt carnallite layer, it is represented by its decomposition products, anhydrite, kieserite, sylvine, and carnallite, formed through the infiltration of liquors rich in magnesium chloride from the carnallite region. Where the carnallite-kieserite layers have undergone hydrothermal change, the conditions may have become favourable for the formation of polyhalite as a secondary deposit. Where hard salt formation has taken place under conditions which would preclude the formation of polyhalite, or where only a purely thermal decomposition of carnallite has occurred, no polyhalite is found. The presence of polyhalite is of great importance from the point of view of chemical genetics.

E. H. R.

The Presence of Boron in some Natural Basic Silico-aluminates. A. LACROIX and A. DE GRAMONT (*Compt. rend.*, 1919, 168, 857—861).—A spectrographic study of three basic silico-aluminates from Madagascar, saphirine, grandidierite, and kornerupine (compare A., 1912, ii, 1182), revealed the presence of boron, and this was confirmed by a further chemical analysis. The boron content of the minerals increased in the order named. The authors consider that boron replaces aluminium isomorphously in these minerals. A number of other silico-aluminates were also examined spectrographically. Boron was found in dumortierite and certain idocrases, whilst in other idocrases its presence was not detected. Similarly, it could not be detected in andalusite, sillimanite, disthene, or in the natural hydrated aluminas examined.

W. G.

Ferrierite, a New Zeolitic Mineral, from British Columbia.

R. P. D. GRAHAM (*Trans. Roy. Soc. Canada*, 1918, [iii], 12, Sect. IV, 185—190).—The mineral occurs in veins of chalcedony and calcite in decomposed basalt on the north shore of Kamloops Lake. It forms white, spherical aggregates of colourless, orthorhombic blades with a perfect pearly cleavage parallel to (100), $D\ 2.150$, $H\ 3-3\frac{1}{2}$, $\alpha\ 1.478$, $\beta\ 1.479$, $\gamma\ 1.482$. Analysis of the transparent blades carefully freed from chalcedony gave:

SiO ₂ .	Al ₂ O ₃ .	CaO.	MgO.	Na ₂ O.	K ₂ O.	H ₂ O.	Total.
69.13	11.44	nil	2.92	3.97	0.36	13.05	100.87

corresponding with Clarke's general formula for ptilolite and mordenite, namely, $Al_2(Si_2O_5)_5R'_4 + 6H_2O$, where $R'_2 = Mg, Na_2, H_2$. Ferrierite, however, differs from all other zeolites in containing magnesium in place of calcium. The mineral commences to lose water at or below 100°; about half is lost at 205°, whilst at 275° 5.71% is still retained, and is probably in part basic.

L. J. S.

Scapolite from the Kiruna District, Swedish Lapland.

NILS SUNDIUS (*Akad. Abhandl. Upsala*, 1915, 197—224, and *Vetenskapliga och praktiska undersökningar i Lappland, anordnade av Luossavaara-Kiirunavaara Aktiebolsg*; from *Jahrb. Min.*, 1918, Ref. 255—257).—The rocks of this district are rich in scapolites, which are very fresh and form fine-grained masses or large, prismatic aggregates. They have been produced by regional pneumatolytic metamorphism, the chlorine, carbon dioxide, and sulphur trioxide having been introduced by magmatic emanations, whilst the other constituents have been derived from the felspars of the pre-existing rocks. Analysis I is of scapolite from amphibolite at Vahåive, II from greenstone at Pahtosvaara, and III from scapolite-diopside-amphibolite at Kalpivaara.

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	Cl.	F.	SO ₃ .	CO ₂ .	Sp. gr.
I. 48.52	27.53	0.25	13.31	1.24	—	—	0.55	n.d.	2.710—2.720
II. 54.82	22.49	—	7.37	3.04	—	—	0.56	n.d.	2.632
III. 57.31	22.07	—	6.27	3.49	0.02	—	0.25	0.34	2.610

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The relation between the optical constants and the composition of these materials is shown in another paper by the same author (this vol., ii, 163).
L. J. S.

Viridine and its Relation to Andalusite. E. A. WÜLFING (*Sitzungsber. Heidelberg. Akad. Wiss., Math.-nat. Kl.*, 1917, *Abh.* 12; from *Jahrb. Min.*, 1918, *Ref.* 259—261).—Viridine from Darmstadt (D 3·220) was described by G. Klemm (*A.*, 1913, ii, 423) as a green variety of andalusite containing Fe_2O_3 4·16 and Mn_2O_3 4·77%, the formula being $(\text{Al,Mn,Fe})_2\text{SiO}_5$, and a similar mineral (D 3·205) from Vestarå, Sweden, was described by H. Bäckström under the name manganandalusite (*A.*, 1897, ii, 271). These are compared optically with the ordinary type of red andalusite (D 3·154) and with greenish-yellow andalusite from Brazil (D 3·162, which has not been analysed, but is probably similar to the red andalusite). Viridine is optically positive with $\gamma=c$, whilst andalusite is optically negative with $a=c$. On account of this difference, viridine is considered to be distinct from andalusite, and consequently Al_2SiO_5 is regarded as tetramorphous, as represented by the minerals kyanite, sillimanite, andalusite, and viridine.
L. J. S.

The Pelham Asbestos Mine, Massachusetts. EARL V. SHANNON (*Amer. Min.*, 1919, 4, 37—39).—Various minerals are developed at the junction of an intrusive mass of peridotite (saxonite) in acid gneiss at this locality. The outer portion of the saxonite is changed to fibrous anthophyllite, which is here mined as asbestos. Associated with biotite is a saponaceous, silvery, bluish-green mineral composed of fine scales; on drying, it becomes opaque and pale olive-green. Analyses I and II of material slightly contaminated with biotite and actinolite prove that this is the "pelhamite" of J. P. Cooke (1875), which is classed by Dana as a vermiculite.

						H_2O <105°.	H_2O >105°.	Total.
	SiO_2 .	Al_2O_3 .	Fe_2O_3 .	CaO .	MgO .			
I.	40·08	21·65	3·59	0·58	20·12	3·79	7·83	97·64
II.	38·88	19·27	3·99	—	22·66	3·36	9·54	97·90

L. J. S.

The Origin of Septarian Structure. W. ALFRED RICHARDSON (*Min. Mag.*, 1919, 18, 327—337).—The origin of the system of polygonal cracks in septarian nodules is discussed in detail. The expansion and contraction theories are dismissed, and it is concluded that the cracks are due to the desiccation of a colloidal centre by chemical means. Similar structures are produced artificially when pats of clay are air-dried or immersed in a concentrated solution of calcium chloride. The following partial analyses are of Ia, the exterior portion, and Ib, the central portion, of an ironstone septarium from the Lias at Bracebridge, Lincolnshire, and II of the clay in which the nodules are embedded.

III of a limestone septarium from Nottinghamshire, *a* the exterior, *b* 1 inch from the outside, and *c* the centre.

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.
Ia.	24·7	18·6	34·3	—
Ib.	13·1	35·1	4·7	22·9
II.	53·1	31·1	7·3	—
IIIa.	12·3	trace	7·2	36·3
IIIb.	8·0	2·0	3·9	45·3
IIIc.	4·5	4·0	3·5	46·0

The nodules probably originated by the rhythmic precipitation of solutions diffusing through a colloid according to Liesegang's laws.

L. J. S.

Analytical Chemistry.

A Simplification of the McLean-van Slyke Method for Estimation of Plasma Chlorides. DONALD D. VAN SLYKE and JOHN J. DONLEAVY (*J. Biol. Chem.*, 1919, **37**, 551—555).—The method previously described (*A.*, 1915, ii, 573) has been simplified by reducing the number of filtrations necessary. The standard silver nitrate solution is made up to contain, in addition to the nitrate, 7.5 grams of picric acid per litre. This solution precipitates both protein and chlorides simultaneously. The excess of silver in the filtrate is titrated with potassium iodide.

J. C. D.

Indirect Electrolytic Estimation of Anions without Platinum Electrodes. E. LASALA (*Anal. Fis. Quim.*, 1919, **17**, 88—95).—The present preliminary investigation is concerned with the estimation of chloride, bromide, and iodide. The halogen is precipitated as silver haloid by means of a 5% solution of silver nitrate. The precipitate is filtered through glass wool and dissolved in 20% solution of potassium cyanide to which a little sodium hydroxide is added. The solution is electrolysed with a nickel-plated copper cathode and a rotating iron anode. Towards the end of the electrolysis, the electrolyte is heated nearly to boiling. The results are most satisfactory. The cathode is prepared by electrolysis of an ammoniacal solution of nickel sulphate.

W. S. M.

Iodometric Studies. The Starch-Iodine Reaction. I. M. KOLTHOFF (*Pharm. Weekblad*, 1919, **56**, 391—404).—A systematic investigation of the sensitiveness of the starch-iodine reaction under varying conditions. The sensitiveness is increased by the presence of salts, especially potassium iodide, and acids (*A.*; 1895, i, 79). Increased temperatures and presence of organic substances

such as alcohols, albumin, etc., diminish the sensitiveness. The magnitude of the correction to be applied in the titration of dilute iodine solutions with dilute thiosulphate solutions, and vice versa, was determined. The correction is a minimum in hydrochloric acid solution to which a little potassium iodide has been added.

W. S. M.

The Iodometric Estimation of Bromate (and Iodate).

I. M. KOLTHOFF (*Pharm. Weekblad*, 1919, **56**, 426—438).—In the titration with thiosulphate solution of bromate solutions to which potassium iodide has been added, the concentrations of bromate and iodide are factors of little importance. It is essential, however, that sufficient acid be present in the mixture. The minimum concentration required in the solution is 0.5*N* for hydrochloric acid and about 1.0*N* for sulphuric acid if titration is carried out immediately after the addition of the iodide. If too little acid is present, oxidation of the thiosulphate directly to sulphate takes place: $8\text{HBrO}_3 + 5\text{H}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O} = 10\text{H}_2\text{SO}_4 + 4\text{Br}_2$ or $4\text{HBrO}_3 + 3\text{H}_2\text{S}_2\text{O}_3 + 3\text{H}_2\text{O} = 6\text{H}_2\text{SO}_4 + 4\text{HBr}$. In either case, too little of the thiosulphate solution is required. The error may be avoided by allowing the mixture to remain some time before titration, or by the addition of a catalyst. The best catalyst is ammonium molybdate in both strong and weakly acid solutions. The catalytic effect of ferrous sulphate and potassium dichromate is negligible in strongly acid solutions, but is more marked in weakly acid solutions. Light has a positive catalytic effect. Salts such as sodium chloride and sodium sulphate retard the reaction.

The reaction between iodate and iodide is much more rapid than that between bromate and iodide, and therefore the iodometric estimation of iodates is not attended by the difficulties arising in the latter case.

W. S. M.

A Simple Form of Apparatus for Estimating the Oxygen Content of Air from the Upper Atmosphere. FRANCIS WILLIAM ASTON (T., 1919, **115**, 472—475).

Sodium Pyrogalloxide Solution as an Absorbent for Oxygen. G. W. JONES and M. H. MEIGHAN (*J. Ind. Eng. Chem.*, 1919, **11**, 311—316).—The rate of oxygen absorption in sodium pyrogalloxide solutions increases with the dilution of the sodium hydroxide; for any given concentration of sodium hydroxide, the rate of absorption is proportional to the concentration of the pyrogallol. Carbon monoxide is evolved from the solution if the sodium hydroxide solution used has a specific gravity of less than 1.30; all sodium pyrogalloxide solutions evolve carbon monoxide if the sample under examination contains more than 95% of oxygen. A reagent which evolves the minimum quantity of carbon monoxide and has a fairly high rate of absorption is made by dissolving sodium hydroxide in its own weight of water and adding five parts

of this solution to two parts of a solution containing 1 gram of pyrogallol in 3 c.c. of water. W. P. S.

The Relation between the Oxygen Concentration and Rate of Reduction of Methylene-blue by Milk. E. NEWTON HARVEY (*J. Gen. Physiol.*, 1919, 1, 415—419).—The rate of reduction and decolorisation of methylene-blue by milk in the presence of an aldehyde is proportional to the oxygen concentration. It is suggested that this fact might be made the basis of a method for determining the oxygen content of gaseous mixtures. Carbon dioxide present in concentrations up to 5% does not affect the reducing action of the milk. J. C. D.

Method for the Identification of Sulphur-Oxygen Compounds. A. SANDER (*Chem. Zeit.*, 1919, 43, 173. Compare A., 1915, ii, 161).—Sulphates, sulphites, hydrogen sulphites, thio-sulphates, sulphides, and polythionates may be identified by their different behaviour towards mercuric chloride, this reagent also serving, to a certain extent, for the identification of the compounds in the presence of each other. The following reactions result when the compounds are treated with an excess of mercuric chloride solution: *Sodium Sulphate*.—Mercuric sulphate and sodium chloride are formed, and the solution remains neutral in reaction. *Sodium Sulphite*.—The solution remains clear and is alkaline towards methyl-orange before and after the addition of mercuric chloride; when the mixture is boiled, it becomes acid and calomel is precipitated. *Sodium Hydrogen Sulphite*.—No precipitate; boiling produces a precipitate and the mixture remains acid. *Sodium Sulphide*.—A black precipitate, which rapidly becomes white owing to the formation of a sulphochloride; the mixture has a neutral reaction before and after boiling. *Sodium Thiosulphate*.—As in the case of a sulphide, a white precipitate forms, but the mixture becomes strongly acid; it remains acid when boiled. *Sodium Polythionate*.—Behaves like sodium thio-sulphate towards mercuric chloride, but may be distinguished from the latter in that it does not decolorise iodine solution and does not give a precipitate of sulphur when acidified. Sulphite and polythionate cannot exist together in the same solution.

W. P. S.

Volumetric Estimation of Sulphurous Acid. THOS. J. I. CRAIG (*J. Soc. Chem. Ind.*, 1919, 38, 96r).—The sulphurous acid solution is added to a known excess of hydrogen peroxide solution acidified with dilute sulphuric acid, and the excess of hydrogen peroxide is then titrated with standardised potassium permanganate solution. The reaction proceeds according to the equations $\text{SO}_2 + \text{H}_2\text{O}_2 = \text{H}_2\text{SO}_4$ and $5\text{H}_2\text{O}_2 + 2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 = \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 8\text{H}_2\text{O} + 5\text{O}_2$. The method may also be applied to solutions containing sulphites or hydrogen sulphites. W. P. S.

Estimation of Total Nitrogen, including Nitric Nitrogen [in Soil Extracts]. B. S. DAVISSON and J. T. PARSONS (*J. Ind. Eng. Chem.*, 1919, **11**, 306—311).—The method recommended consists in boiling the soil extract solution with a quantity of sodium hydroxide sufficient to make the alkalinity approximately $N/10$, reduction of the nitric nitrogen being effected by the addition of Devada's alloy. The boiling flask is connected with an absorption tube containing an excess of sulphuric acid (4:1). The contents of the absorption tube are then washed into the flask, the mixture is evaporated until charring commences, potassium sulphate is added, and the digestion continued. The ammonia formed is distilled after the addition of sodium hydroxide and sodium sulphide. [See, further, *J. Soc. Chem. Ind.*, 1919, 332A.]
W. P. S.

Estimation of Nitrous Acid and Nitrites. J. S. LAIRD and T. C. SIMPSON (*J. Amer. Chem. Soc.*, 1919, **41**, 524—531).—The volumetric methods for the estimation of nitrous acid and nitrites, as described in the literature, have been experimentally examined and shown to be unsatisfactory. The authors have devised a method for estimating nitrites which consists in the oxidation of the nitrite in acid solution with excess of potassium permanganate, reduction of the excess of permanganate by an excess of ferrous sulphate, sodium oxalate, or hydrogen peroxide, and titration of the excess of the reducing agent by permanganate. In the actual estimation, the nitrite is run slowly into the excess of permanganate, acidified with 1:4-sulphuric acid, and constantly shaken. The titration is not interfered with by moderate amounts of chloride or small amounts of bromide. Silver nitrite is not a satisfactory material for use as a standard in nitrite estimations. A satisfactory standard solution may be made by titrating sodium nitrite solution with potassium permanganate according to the method described above or sodium nitrite solution may be standardised gravimetrically by the reduction of silver bromate to silver bromide according to Busvold's method (*A.*, 1914, ii, 144).
J. F. S.

Gravimetric Estimation of Phosphoric Acid as Magnesium Pyrophosphate. Z. KARAOGLANOW (*Zeitsch. anal. Chem.*, 1918, **57**, 497—541).—An investigation of the different methods employed for the precipitation of phosphoric acid as ammonium magnesium phosphate previous to the conversion of the precipitate into magnesium pyrophosphate. To a slight extent, the precipitation depends on temperature, rate of precipitation, and presence of varying quantities of magnesium chloride, ammonium chloride, etc. the differences in the final results are usually very small. The lack of a more trustworthy method for the estimation of phosphoric acid and the difficulty of obtaining a substance of known phosphorus content render it impossible to say which method of precipitation gives the true quantity of phosphoric acid present.
W. P. S.

Gravimetric Analysis. X. XII. Estimation of Phosphoric Acid. L. W. WINKLER (*Zeitsch. angew. Chem.*, 1919, **32**, 98—101).—Precipitation of phosphoric acid as ammonium magnesium phosphate and weighing it as such or after ignition to magnesium pyrophosphate, yields trustworthy results. The presence of large quantities of potassium and sodium chlorides does not influence the results when the precipitate is weighed in the form of ammonium magnesium phosphate, but when the precipitate is converted into pyrophosphate, the result is too high if potassium chloride was present in the solution. [See, further, *J. Soc. Chem. Ind.*, 1919, 391A.] W. P. S.

Estimation of Arsenic in Volatile Cacodyl Compounds. L. C. MAILLARD (*Bull. Soc. chim.*, 1919, [iv], **25**, 192—200).—The method is based on the oxidation of the cacodyl compound to cacodylic acid, and subsequently to arsenic acid. The arsenic is then separated in the usual manner by precipitation as magnesium ammonium arsenate, and weighed as pyroarsenate. For the first stage of the oxidation, a suitable weight of the cacodyl compound, in a sealed bulb if liquid or in a narrow tube if solid, is introduced into a flask containing 3 grams of ammonium persulphate, 30 c.c. of water, and 10 c.c. of sulphuric acid. The flask is quickly closed with a ground-in stopper and thoroughly shaken until the air in the flask, at first cloudy, is quite clear. Ten c.c. of fuming nitric acid are now added, and the estimation proceeded with in the usual way, the arsenic being first precipitated as its sulphide if necessary and then redissolved before finally precipitating it as the double arsenate. The method was applied to cacodyl chloride, and found to be simple and accurate. W. G.

Gravimetric Analysis. XI. XIII. Estimation of Arsenic Acid. L. W. WINKLER (*Zeitsch. angew. Chem.*, 1919, **32**, 122—124).—Two methods are described for the estimation of arsenic acid. In the first, the arsenic acid is treated with potassium thiocyanate, then with hydrogen sulphide, and the precipitate, consisting of arsenic trisulphide and sulphur, is collected, dried at 100°, and weighed: $\text{As}_2\text{O}_5 + 2\text{KCNS} = 2\text{KOCN} + \text{As}_2\text{O}_3 + \text{S}_5$; $\text{As}_2\text{O}_3 + 3\text{H}_2\text{S} = \text{As}_2\text{S}_3 + 3\text{H}_2\text{O}$. The second method consists in the precipitation of the arsenic acid as ammonium magnesium arsenate; details of the procedure are given in full. Arsenious acid solutions may be oxidised by hydrogen peroxide in the presence of ammonia, and the arsenic then precipitated as ammonium magnesium arsenate. [See, further, *J. Soc. Chem. Ind.*, 1919, June.] W. P. S.

Selection of an Indicator for the Acidimetric Estimation of Boric Acid. JOHANNES PRESCHER (*Zeitsch. Nahr. Genussm.*, 1918, **36**, 283—286).—Phenolphthalein is considered to be the most suitable indicator for the purpose. W. P. S.

Electrical Precipitator for Analysing Smokes. RICHARD C. TOLMAN, L. H. REYERSON, A. P. BROOKS, and H. D. SMYTH (*J. Amer. Chem. Soc.*, 1919, **41**, 587—589).—A modified form of the Cottrell precipitator is described which has been used for removing the solid particles from smokes. The apparatus consists of a glass tube 1.6 cm. in diameter and 25 cm. long, a thin aluminium foil cylinder 0.025 mm. thick is placed in the glass tube and constitutes the anode, and a cathode consisting of a No. 25 platinum wire threaded with a jeweller's die passes centrally down the aluminium cylinder. Entrance and exit tubes for the smoke are attached at the ends. A high-voltage circuit (15,000 volts) is attached to the electrodes, and a corona discharge produced; sparking must be avoided. The smoke is then admitted at the rate of 5 litres per minute, when the negatively charged particles are deposited on the aluminium foil. The weight of particles is determined by weighing the anode before and after the precipitation. J. F. S.

Characterisation and Estimation of Carbonyl Chloride. ANDRÉ KLING and RENÉ SCHMUTZ (*Compt. rend.*, 1919, **168**, 773—775).—Carbonyl chloride readily reacts with an excess of aniline in saturated aqueous solution to give diphenylcarbamide and aniline hydrochloride. Thus a trace of carbonyl chloride in air may readily be detected by bubbling 5 litres of the air at the rate of 1 litre in five minutes through the aqueous solution of aniline, and characterising the precipitate microscopically and by its m. p. as diphenylcarbamide, which is practically insoluble in water. By this means, carbonyl chloride may be detected in the air at a dilution of 1 in 100,000. For the estimation of carbonyl chloride in solution in organic solvents, a quantity of the solution containing 0.2—0.35 gram of carbonyl chloride is added to 150 c.c. of the aqueous aniline solution (containing 26 grams of aniline per litre), and after two hours the mixture is heated on a water-bath for one hour to drive off the organic solvent. The liquid is allowed to cool, and the next day the precipitate of diphenylcarbamide is collected on a Gooch crucible, dried at 70°, and weighed. W. G.

Estimation of Traces of Carbonyl Chloride in Air. ANDRÉ KLING and RENÉ SCHMUTZ (*Compt. rend.*, 1919, **168**, 891—893).—Using the method previously described (preceding abstract), the carbonyl chloride may be estimated gravimetrically if the weight of diphenylcarbamide exceeds 10 mg. by dissolving the precipitate off the filter with alcohol and evaporating the alcoholic solution in a weighed platinum crucible at a temperature not exceeding 60°, after which the residue is dried at this temperature for two hours. Alternatively, a colorimetric method may be employed by digesting the precipitate and filter paper with sulphuric acid and mercuric sulphate, and proceeding as in the ordinary Kjeldahl process, the ammonia passing over being collected in *N*/250-hydrochloric acid, and finally estimated by means of Nessler's reagent. W. G.

Analyses of Mixtures of Vapours containing Carbon Monoxide, Carbon Dioxide, Carbonyl Sulphide and Carbon Disulphide and similar Mixtures of Gases. ALFRED STOCK and PAUL SEELIG (*Ber.*, 1919, **52**, [B], 672—680. Compare Stock and Kuss, A., 1917, ii, 205).—The processes described depend on the difference in the rates with which the various gases or vapours are absorbed by alkali.

Carbon dioxide is immediately absorbed by alkali hydroxides of widely differing concentrations. Carbonyl sulphide is absorbed by the hydroxides of rubidium, potassium, sodium, and lithium in order of decreasing rapidity; with sodium hydroxide, the rate of absorption varies with the concentration, being at a minimum with a 30% solution; the gas is completely absorbed in about an hour. The complete absorption of carbon disulphide vapour by aqueous alkali hydroxide requires several days, whilst carbon monoxide is not absorbed.

An alternative method of estimating carbon disulphide in gaseous mixtures, which can be rapidly and accurately performed, consists in saturating a measured volume of the gas with carbon disulphide and measuring the increase in volume.

Two methods are described for the analysis of the mixture. (1) A measured volume of the gas is shaken with sodium hydroxide solution (30%, 1 c.c.), and the volume read off each minute during several minutes (CO_2). Water (4 c.c.) is now added, and the gas volume is determined every ten minutes for about an hour (COS). Potassium hydroxide (30%, 1 c.c.) is now added, and the volume recorded after one, two, three, etc., days (CS_2). The residue is carbon monoxide, which must be completely absorbed by cuprous chloride solution. (2) Carbon dioxide is estimated in one portion as usual. A second portion is intermittently shaken with sodium hydroxide (2—3 c.c., 50%); after fifteen to thirty minutes, shaking is made continuous, and the volume read off each minute until it is constant ($\text{CO}_2 + \text{COS}$). A third portion is shaken occasionally with potassium hydroxide (5%, 2—3 c.c.), and the volume determined daily until constant ($\text{CO}_2 + \text{COS} + \text{CS}_2$), the residual carbon monoxide being tested for purity by means of ammoniacal cuprous chloride solution. Alternatively, the residue obtained after absorption of CO_2 and COS may be saturated with carbon disulphide and the increase in volume determined.

The paper also contains a vapour tension-temperature table for aqueous sodium hydroxide solutions of differing concentration and for carbon disulphide, for which the data given in the literature are somewhat discordant. H. W.

Estimation of Alkali in Permanganate Liquors. THOS. J. I. CRAIG (*J. Soc. Chem. Ind.*, 1919, **38**, 96—97T).—The method depends on the reaction between permanganate and hydrogen peroxide, $5\text{H}_2\text{O}_2 + 2\text{KMnO}_4 = 2\text{KOH} + 2\text{MnO}_2 + 4\text{H}_2\text{O} + 4\text{O}_2$. After filtration, the alkalinity is estimated by titration; the alkalinity due to the permanganate is deducted from the result, and the

remainder represents the quantity of free alkali (hydroxide or carbonate) in the solution. With manganates, the reaction proceeds according to the equation $\text{H}_2\text{O}_2 + \text{Na}_2\text{MnO}_4 = 2\text{NaOH} + \text{MnO}_2 + \text{O}_2$. In analysing mixtures containing both permanganate and manganate, the proportions of these compounds may be found by treating a portion of the solution with carbon dioxide or sodium hydrogen carbonate to convert the manganate into permanganate, $3\text{Na}_2\text{MnO}_4 + 2\text{CO}_2 = 2\text{NaMnO}_4 + 2\text{Na}_2\text{CO}_3 + \text{MnO}_2$; the precipitated manganese dioxide (which contains manganese equivalent to one-third of the manganate) is collected, and its quantity estimated by titration with ferrous sulphate and permanganate solutions.

W. P. S.

Conditions affecting the Precise Estimation of Zinc as the Sulphide. HAROLD A. FALES and GERTRUDE M. WARE (*J. Amer. Chem. Soc.*, 1919, **41**, 487—499).—The conditions affecting the quantitative estimation of zinc as sulphide have been investigated. It is shown that a hydron concentration lying between 10^{-2} and $10^{-3}N$ is most favourable for the quantitative precipitation of zinc sulphide in a form suitable for rapid filtration and washing. The concentration of the hydron may be kept within this range by the use of ammonium citrate or a mixture of ammonium sulphate, ammonium formate, and formic acid. The precipitation of granular zinc sulphide is favoured, not only by a concentration of hydron within the above-mentioned limits, but also by a high concentration of an ammonium salt of a strong acid, by a concentration of 1 gram of zinc per litre of solution, and by a temperature of 95—100°. It is desirable that the hydrogen sulphide should be passed in under pressure for the purpose of obtaining rapid saturation and avoiding loss of formic acid by evaporation. The authors recommend the following method of procedure. The zinc solution, which has been freed from cadmium, copper, and other elements likely to be precipitated, is evaporated to 125 c.c. and treated with ammonium hydroxide until the precipitate at first formed fails to redissolve, 25 c.c. of a citrate solution (200 grams of citric acid per litre of water neutralised by 15*N*-ammonia) are added, and the whole solution is made neutral to methyl-orange with ammonia. Then 25 c.c. of formic acid mixture (30 c.c. of 15*N*-ammonium hydroxide, 200 c.c. of 13.6*N*-formic acid and 250 grams of ammonium sulphate in 1000 c.c. of water) are added, and the whole is made up to 200 c.c. The solution is heated to 60° and connected with a hydrogen sulphide generator, so that air is slowly expelled from the flask as the heating is continued. At 90—100°, the flask exit is closed, and the solution as it cools saturated with hydrogen sulphide under increasing pressure. The flask should be shaken frequently to ensure saturation, which is usually complete when the precipitate settles rapidly. The precipitate is filtered and washed with a cold 0.1*N*-solution of formic acid saturated with hydrogen sulphide. The precipitate is transferred to a weighed porcelain crucible and

the filter paper charred. The completion of the ignition of the filter paper should be carried out in an oxidising atmosphere, and the reaction should proceed so that the sulphide is converted into sulphate and not into oxide. After cooling, the precipitate is moistened with concentrated sulphuric acid and heated in an air bath until the excess of acid is expelled, and then heated over a flame to remove any charred material. The mass is again moistened with sulphuric acid and heated in the air to expel the excess of acid, allowed to cool in a desiccator, and weighed. The last process is repeated until a constant weight is obtained. A modification of the above process is described which enables zinc to be quantitatively separated from iron, manganese, nickel, and cobalt. The processes described are accurate to one part per thousand.

J. F. S.

Separation of Lead in Metallic Calcium and "Lurgie"

Metal. J. KÖNIG (*Chem. Zeit.*, 1919, **43**, 135).—The metal is dissolved in nitric acid, the solution neutralised with ammonia, treated with an excess of bromine-water, then rendered ammoniacal, cooled, and filtered. The lead is thus removed completely, and the calcium may be estimated in the filtrate by precipitation as oxalate. In the case of "lurgie" metal, barium must be separated as sulphate before the calcium is precipitated. [See, further, *J. Soc. Chem. Ind.*, 1919, 370A.]

W. P. S.

The Electrolytic Estimation of Mercury without Platinum Electrodes. J. GUZMÁN and P. POCH (*Anal. Fis. Quím.*, 1918, **16**, 742—755).—*Estimation in Nitric Acid Solution.*—A copper cathode and a graphite anode are used. The cathode is plated with a brilliant deposit of silver from cyanide solution, and is then washed successively in boiling water, alcohol, and ether. The mercury solution must be only slightly acid, and in order to preserve the anode, the voltage must not exceed three volts. The electrolysis is carried out in the cold. By this method, results with a maximum error of 0.3% are obtained. A similar procedure with mercuric chloride solution gives results which are less satisfactory. Excellent results are obtained with the silvered cathode and a fine platinum spiral as anode, and also with a copper cathode plated with copper by electrolysis in copper sulphate solution acidified with nitric acid. The presence of the chlorine ion is detrimental. The copper cathode may be used seven or eight times, but after every analysis the mercury must be removed by heating, and the silver with cyanide solution.

Estimation in Ammoniacal Solution.—The anode is of iron which has been heated to redness and allowed to cool in the air. A voltage of 2.4 volts is employed. The copper cathode is first nickel-plated and then covered with a deposit of silver. It is found that, after the first analysis, the employment of the same cathode, even after re-plating, gives results which are no longer quantitative, as the mercury forms a grey powder on washing with

alcohol. The same difficulty is found with cathodes on which had been deposited protective layers of gold, tin, or bismuth. The only cathode which can be used repeatedly is of copper with a deposit of mercury from electrolysis in mercuric nitrate solution. The deposit must be polished by brushing after each determination. The electrolysis is carried out in mercuric nitrate solution to which has been added ammonium nitrate and concentrated ammonia solution. The method is accurate within 0.3%.

Estimation in Alkaline Cyanide Solution.—In this case, the cathode is of copper with a brilliant deposit of silver, and the anode of iron. Sodium hydroxide solution in excess is added to a mercuric nitrate solution, and then just sufficient potassium cyanide to dissolve the precipitate formed. This electrolyte is maintained at 50° during the electrolysis. Voltage, 2.5 volts. The maximum error observed is less than 0.2%. Satisfactory results are obtained by this method in presence of the chlorine ion if the iron anode is replaced by graphite. The method is applicable to the analysis of commercial products containing mercury.

Estimation in Alkaline Sulphide Solution.—The electrolyte is prepared by dissolving precipitated mercuric sulphide in sodium sulphide solution and adding sodium hydroxide solution. With a cathode of amalgamated copper and an anode of iron, the results are moderately satisfactory, but the cathode cannot be used for a repetition of the analysis even after brushing. The addition of potassium cyanide and carbamide to the electrolyte does not lead to any marked improvement in the results. W. S. M.

Gravimetric and Volumetric Estimation of Mercury Precipitated as Mercury Zinc Thiocyanate. GEORGE S. JAMIESON (*J. Ind. Eng. Chem.*, 1919, **11**, 296—297).—A solution of a mercuric salt or compound (containing about 0.14 gram of mercury) is treated with 25 c.c. of a solution containing 39 grams of ammonium thiocyanate and 29 grams of zinc sulphate per litre. The precipitate of mercury zinc thiocyanate formed is collected, washed with a solution prepared by diluting 5 c.c. of the thiocyanate reagent with 450 c.c. of water, dried at 105°, and weighed. The weight of the precipitate is multiplied by 0.40258 to obtain the quantity of mercury present. The volumetric method consists in treating the moist precipitate with 35 c.c. of concentrated hydrochloric acid, 10 c.c. of water, and 7 c.c. of chloroform, and titrating the mixture with standardised potassium iodate solution. [See, further, *J. Soc. Chem. Ind.*, 1919, 341A.] W. P. S.

Estimation of Uranium in Alloy Steels and Ferro-uranium. G. L. KELLEY, F. B. MEYERS, and C. B. ILLINGWORTH (*J. Ind. Eng. Chem.*, 1919, **11**, 316—317).—The sample is dissolved in hydrochloric acid, nitric acid is added, and silica and tungstic acid are separated; the greater part of the ferric chloride is then removed by extraction with ether, the solution is boiled with the addition of an excess of sodium carbonate, and filtered.

The filtrate, containing the uranium together with molybdenum and vanadium, is acidified with sulphuric acid, boiled, rendered ammoniacal, and again boiled. Uranium and some vanadium are precipitated; the precipitate is heated with ammonium carbonate solution, the mixture filtered to remove traces of manganese, iron, etc., and the filtrate acidified with sulphuric acid, boiled, and the uranium and vanadium reprecipitated by ammonia. The precipitate is collected, ignited, and weighed. The small quantity of vanadium it contains is estimated by titration with permanganate solution after solution in hydrochloric acid, or by oxidation with ammonium persulphate and silver nitrate, followed by electrometric titration. [See, further, *J. Soc. Chem. Ind.*, 1919, June.]

W. P. S.

Analysis of Natural Gas and the Calculation and Application of Results. R. P. ANDERSON (*J. Ind. Eng. Chem.*, 1919, **11**, 299—306).—An indicator is described for showing complete combustion of the sample when the natural gas is passed slowly into oxygen in which an electrically heated platinum spiral is glowing; this indicator consists of a narrow glass tube connected by means of a T-piece with the rubber tubing connecting the combustion pipette with the levelling bulb; when the gas has been passed into the pipette, the tap on the levelling bulb is closed, and the contractions of the gases in the pipette are shown by the fall of the level of mercury in the narrow tube. When this fall ceases, combustion is complete. The combustion pipettes should be made of Pyrex glass. Calculation of results of combustions of natural gas according to theoretical equations is discussed, and tables of correction factors are given.

W. P. S.

Detection of Methyl Alcohol. E. SALKOWSKI (*Zeitsch. Nahr. Genussm.*, 1918, **36**, 262—270).—Tests which depend on the oxidation of the methyl alcohol by potassium permanganate and on the detection of the formaldehyde produced are fairly trustworthy when applied to mixtures of methyl alcohol and pure ethyl alcohol, since the latter does not yield formaldehyde. Higher alcohols (propyl, isobutyl, and isoamyl), however, yield distinct quantities of formaldehyde when oxidised by permanganate; the colorations obtained are less intense than those yielded by methyl alcohol, and the tests may be used, with due caution, for the detection of methyl alcohol in ethyl alcohol. Only small quantities of higher alcohols are likely to be present in commercial alcohol, whilst alcohol deliberately adulterated with methyl alcohol usually contains not less than 10% of the latter. [See, further, *J. Soc. Chem. Ind.*, 1919, 382A.]

W. P. S.

[A Case of Poisoning by Methyl Alcohol and] a Simple Method of Distinguishing between Methyl Alcohol and Absolute Ethyl Alcohol or Spirit. TH. SABALITSCHKA (*Ber. Deut. pharm. Ges.*, 1919, **29**, 214—219).—In connexion with a

case of poisoning due to the substitution of methyl alcohol for ethyl alcohol, the author has elaborated the following method for distinguishing between these substances. The specimen (2 c.c.) is frequently shaken during ten minutes with powdered crystalline copper sulphate (0.1 gram), and the solution is filtered. The filtrate is treated with water (5 c.c.) and ammonia solution (10%, 3 c.c.); with methyl alcohol, a deep blue to blue coloration is developed, whilst with ethyl alcohol the solution is only coloured a faint, pale blue. The method may also be used to obtain an approximate estimation of methyl alcohol in mixtures of the latter with absolute alcohol, providing the content is not less than 20%; if this is the case, the specimen must be distilled and the test performed on the first portion of the distillate. In the presence of water, even in small quantities, the process is useless, since the solutions of hydrated salts in alcohol are unstable, and the presence of water promotes separation of the salt.

Copper sulphate may also be replaced by crystalline ferrous sulphate. In this case, separation of the salt occurs with greater readiness, and the sample should only be shaken with the sulphate for five minutes. The presence of iron in the filtrate is detected by addition of water (5 c.c.) and 2.5% potassium ferricyanide solution (2 c.c.), the colorations obtained ranging from dark blue with methyl alcohol to pale green with ethyl alcohol. H. W.

Estimation of Ethyl Ether in Blood. J. W. LE HEUX (*Zeitsch. physiol. Chem.*, 1919, **104**, 137—140).—The method of Nicloux ("Les Anesthésiques Généraux," Paris, 1908) has been modified so as to increase the accuracy. Ten c.c. of blood are mixed with 65 c.c. of a saturated solution of picric acid, and the ethyl ether removed by distillation. The ether in the distillate is quantitatively oxidised to acetic acid by chromic acid, and the excess of chromic acid determined by the iodometric method. J. C. D.

A New Method for Estimating small amounts of Dichloroethyl Sulphide (Mustard Gas). E. F. HOPKINS (*J. Pharm. Expt. Ther.*, 1919, **12**, 393—403).—See this vol., i, 250.

Estimation of the Different Constituents of a Mixture containing Eugenol, Triacetin, and Benzyl Alcohol. H. PERPEROT (*Ann. Chim. anal.*, 1919, [ii], **1**, 112—114).—The quantity of triacetin is calculated from the saponification number of the mixture, whilst the iodine number is a measure of the amount of eugenol present. A portion of the mixture is also acetylated in the usual way, and the saponification number of the acetylated product is estimated; after deducting the amount due to triacetin and acetylated eugenol, the remainder is a measure of the acetylated benzyl alcohol. [See, further, *J. Soc. Chem. Ind.*, 1919, 387A.] W. P. S.

Estimation of Thymol. E. MOLES and M. MARQUINA (*Anal. Fis. Quím.*, 1919, **17**, 59—83).—See this vol., i, 270.

Estimation of small Quantities of Acetone, Alcohol, and Benzene in Air. S. ELLIOTT and J. DALTON (*Analyst*, 1919, **44**, 132—136).—The air under examination is aspirated through four absorption cylinders fitted with Folin tubes (*J. Biol. Chem.*, 1912, **11**, 493) connected by means of long rubber tubing with siphon bottles. For the estimation of acetone, one of the absorption vessels is charged with standard iodine and sodium hydroxide solutions, and the excess of iodine subsequently titrated, as in Messinger's method (A., 1889, 313). No appreciable amount of iodoform is formed by the alcohol vapour in the air if the temperature is kept low. Alcohol is estimated by Szeberényi's method (A., 1915, ii, 292) of oxidising it to acetic acid by means of a mixture of potassium dichromate and dilute sulphuric acid, whilst Pfeiffer's method (A., 1904, ii, 786), in which the benzene is nitrated by means of a mixture of nitric and sulphuric acids, gives trustworthy results. In this case, the fourth absorption vessel is charged with sodium hydroxide solution and interposed between the acid absorption vessel and the siphons to protect the tubing. The minimum and maximum amounts of these substances per million c.c. found in the air of factories were: acetone, 0.02 to 1.86 grams, whilst the mean amount found was 0.31 gram; alcohol, 0.02 to 3.00, with a mean of 0.65 gram; benzene, 0.01 to 0.90, with a mean of 0.26 gram. [See also *J. Soc. Chem. Ind.*, 1919, 342A.]
C. A. M.

Application of the Grimbart-Leclère Reaction of apo-Morphine to Alkaloids and Adrenaline. G. DENIGÈS (*J. Pharm. Bordeaux*, 1918, **56**, 185; from *J. Pharm. Chim.*, 1919, [vii], **19**, 49).—The reaction described by Grimbart and Leclère (A., 1915, ii, 192) is also given by morphine under the following conditions. A few mg. of the alkaloid are heated with 2 drops of sulphuric acid until a slight brown coloration appears; the mixture is then diluted with 5 c.c. of saturated sodium acetate solution, 2 drops of 4% mercuric chloride solution are added, and the mixture is boiled. A green coloration is obtained. Catechol, when boiled with sodium acetate and mercuric chloride, yields a reddish-violet substance, which is soluble in ether, chloroform, and amyl alcohol. Adrenaline, treated similarly, but not heated above 50°, gives a red coloration; the reaction may be obtained with as little as 0.01 mg. of adrenaline.
W. P. S.

Estimation of the Non-Protein Nitrogenous Constituents of Milk. W. DENIS and A. S. MINOT (*J. Biol. Chem.*, 1919, **37**, 353—366).—For the estimation of total non-protein nitrogen in cows' milk, the protein and fat are removed by heating in the presence of copper sulphate. The filtrate is treated with formaldehyde, which prevents the precipitation of amino-acids as insoluble copper compounds during the subsequent removal of the lactose with cupric hydroxide. For the latter process, calcium hydroxide is preferred to sodium hydroxide, as any excess of calcium may be removed as oxalate. The total nitrogen is

estimated by conversion into ammonia with subsequent Nesslerisation (Folin and Denis, A., 1916, ii, 573). Slight modifications of this method are described for the analysis of human milk. Urea in milk may be determined by the urease method (Marshall, A., 1913, ii, 640). Ten c.c. of human or 5 c.c. of cow's milk are treated with 2 c.c. of an extract of Jack bean for thirty minutes. The ammonia produced is carried over into standard acid by a stream of air and estimated by Nesslerisation.

In the estimation of creatine and creatinine, protein may be removed by metaphosphoric acid. The presence of lactose, however, intensifies the colour reaction with picric acid, and if this method is used, equivalent amounts of the sugar should be added to the standard solution. It is perhaps better to remove protein, fat, and lactose by copper sulphate and calcium hydroxide, and to apply the colour reaction to the clear, sugar-free filtrate. Amino-nitrogen is determined by the nitrous acid decomposition method of Van Slyke (A., 1912, ii, 1008). Protein must first be removed by precipitation with acetic acid and copper acetate. For the determination of uric acid, advantage is taken of the method described by Morris (A., 1916, ii, 456). The milk is treated with acetic acid and zinc acetate solution, and heated on the water-bath for fifteen to twenty minutes. After cooling and making up to a known volume, it is filtered, and an aliquot part of the filtrate treated with zinc acetate and sodium carbonate solution. The resulting precipitate is separated by centrifugalisation, washed, treated with acetic acid, and the zinc removed by hydrogen sulphide. Uric acid in the concentrated filtrate is estimated by the colour reaction with Folin and Denis's reagent (A., 1912, ii, 1011). Estimations of these non-protein nitrogenous constituents in cow's milk and human milk are given.

J. C. D.

A Multiple Pipette Holder for the Distribution of Serum for the Complement-fixation Test. FRANCOIS. H. REYNOLDS (*J. Agric. Res.*, 1918, 15, 615—618).—The pipette holder consists of a brass tube 35 cm. long and 0.94 cm. external diameter, the two ends being closed by screws or caps, and having twelve side-tubes set in one plane perpendicular to it at equal intervals along it. Another tube, to serve as a mouthpiece, is fixed on the opposite side to these tubes. The twelve side-tubes, each being 0.6 cm. in internal diameter, are lined with rubber tubing, of which the free end is folded back over the mouth of each tube, and into these are inserted the graduated pipettes. In this way, twelve lots of serum may be withdrawn at once.

W. G.

General and Physical Chemistry.

Ultra-violet Band of Ammonia and its Occurrence in the Solar Spectrum. A. FOWLER and C. C. L. GREGORY (*Phil. Trans.*, 1919, [A], 218, 351—372. Compare A., 1918, ii, 282).—The ammonia spectrum has been photographed (i) by means of a quartz spectrograph giving a dispersion of 60 Å. per mm. at λ 3360, (ii) by a quartz Littrow instrument having a dispersion of 7 Å. per mm., and (iii) by means of a 10 ft. grating giving a dispersion of 1.85 Å. per mm. In the first two cases an ammonia flame was used, obtained by feeding a blowpipe with ammonia and oxygen, whilst in the last case a copper arc burning in ammonia furnished the light. Long tables of wave-lengths are given, which are probably accurate to 0.01 Å.; these are compared with the Rowland values for the solar spectrum. From the comparison, it is evident that the band $\lambda=3360$ in the solar spectrum is due to ammonia, and also that many of the unidentified weaker lines of the solar spectrum are also due to ammonia. Photographs of the highly resolved band λ 3360 are appended to the paper. J. F. S.

Wave-length Measurement in Spectra from 5600 Å. to 9600 Å. W. F. MEGGERS (*Bull. Bureau of Standards [U.S.A.]*, 1918, 14, [3], 371—395).—The first-order spectra of lithium, sodium, potassium, rubidium, caesium, copper, glucinum, calcium, strontium, barium, and magnesium have been photographed over the long wave regions 5600 Å. to 9600 Å. For this purpose, a concave grating of radius of curvature 640 cm. with a ruled surface 7.5 cm. by 13.3 cm. with 299 lines per mm. was employed, and was mounted in parallel light, the intensity of the spectra, compared with that afforded by the Rowland method of mounting, being quadrupled by this method of mounting. The device also secures freedom from astigmatism. Ordinary photographic plates are sensitised to the long wave region by being soaked for three to five minutes in a bath made by adding 4 c.c. of a solution of 1 part of dicyanin in 1000 parts of alcohol to 50 c.c. of distilled water, 50 c.c. of ethyl alcohol, and 5 c.c. of strong ammonia. The exposures were limited to thirty minutes. Arcs of metallic electrodes were employed wherever possible, Acheson graphite electrodes impregnated with large quantities of the respective salts being employed in other cases. A current of 6 amperes was employed for the region 6000 Å. to 7000 Å., 7 amperes for the region 7000 Å. to 8000 Å., and so on, except in the case of magnesium, a current of 3 amperes at 110 volts being employed in this case. The comparison spectra were afforded by that of an arc between Norwegian iron poles operated under standard conditions. The results obtained are expressed in tabular form, which afford ready comparison with the results of other observers. The intensities and other physical characteristics of the various lines are recorded. Illustrations of the spectra are

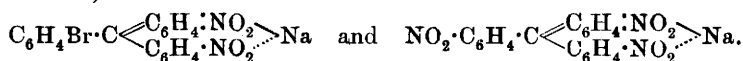
given in some cases. The probable error is less than 0.02 Å. for all lines measured more than twice. The frequency differences of doublets in the spectra of sodium, potassium, rubidium, caesium, and copper are shown to be constant in most cases to 1 part in 100,000 in the number of waves per cm. J. S. G. T.

The Serial Constitution of Absorption Spectra. FRED. VLÈS (*Compt. rend.*, 1919, **168**, 1044—1047).—A continuation of previous work (compare A., 1914, ii, 400) in which the author, from a study of the absorption spectra of several substances, confirms his views as to the serial constitution of these spectra.

W. G.

Absorption and Constitution of the Coloured Alkali Salts of Nitrotriphenylmethanes and Related Compounds. A. HANTZSCH and F. HEIN (*Ber.*, 1919, **52**, [B], 493—509. Compare A., 1907, i, 500; and Hedley, 1908, i, 382).—A comparison of the alkali salts of nitrotriphenylmethanes and nitrodiphenylamines, nitrohydrazobenzenes, and nitrodiazoaminobenzenes.

Triphenylmethane only forms a mono- and a tri-nitro-derivative. Diphenyl-*p*-tolylmethane (from benzhydrol and toluene by means of stannic chloride) reacts with fuming nitric acid to give 4:4'-dinitro-diphenyl-*o*-nitro-*p*-tolylmethane, m. p. 131°. *p*-Bromotriphenylmethane, however, gives 4-bromo-4':4''-dinitrotriphenylmethane, white leaflets, m. p. 165.5°. The salts of nitrotriphenylmethanes are much less stable than those of the simple nitromethanes, and can scarcely be isolated. Solutions of the mononitro-compounds in alcohol remain colourless for a moment on the addition of sodium ethoxide, but reach the maximum yellow colour in about fifteen minutes. The absorption bands are similar to those of the mononitromethane *aci*-salts, but include a quinonoid band, showing that the salts have the simple quinonoid, as well as the *aci*-configuration, thus: $\text{CHPh}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2 + \text{EtONa} \rightarrow \text{CPh}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO} \cdot \text{ONa}$. The dinitro- and trinitro-compounds give violet salts, which have the "conjugated-quinonoid" configuration of the di- and tri-nitro-methanes, thus:



They also give violet salts with ammonia and aliphatic amines, but not with pyridine.

[With M. HARDTMANN].—*p*-Nitrodiphenylamine is best obtained by nitrating pure benzoyldiphenylamine and then hydrolysing by means of alcoholic potassium hydroxide. Its solution in alcohol is pale yellow, but becomes deep red on the addition of potassium hydroxide, owing to the formation of a para-quinonoid salt of the formula $\text{NPh} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2 \cdot \text{K}$. The *o*-nitrodiphenylamine is yellowish-red in alcoholic solutions, but the addition of potassium hydroxide has no effect. *p*:*p'*-Dinitrodiphenylamine, like the di-, tri-, and hexa-nitrotriphenylmethanes, gives deep violet salts. Strange to say, the salts of hexanitrodiphenylamine are only yellowish-red.

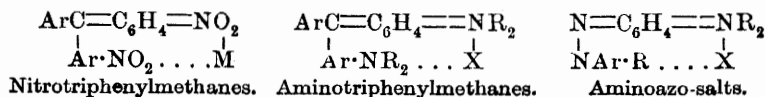
p-Nitrodiazoaminobenzene, *pp'*-dinitrohydrazobenzene, and *pp'*-nitrodiazoaminobenzene also give violet salts. The last compound is obtained by the action of amyl nitrite on *p*-nitroaniline, but a drop of acetic acid is essential to the initiation of the reaction. Its sodium salt, $C_{12}H_8O_4N_5Na$, separates on cooling a solution in aqueous-alcoholic sodium hydroxide, in leaflets with metallic lustre and red streak, which are hydrolysed by cold water to the free *ac*-dinitrodiazoaminobenzene, $NO_2 \cdot C_6H_4 \cdot N:N:N:C_6H_4 \cdot NO \cdot OH$. This looks so much like the salt that it has previously been unrecognised. It is even formed when dilute solutions of the ordinary dinitro-compound are boiled and quickly cooled, but it is immediately isomerised by alcohol. When slowly heated, it changes into the more stable form and then explodes at about 233° .

Absorption curves are reproduced in the original and discussed at some length partly in a controversial manner. J. C. W.

Absorption and constitution of the Simplest Triphenylmethane- and Azo-Dyes and Related Compounds. A. HANTZSCH (*Ber.*, 1919, 52, [B], 509—530).—The absorption bands of the simplest and most important dyes, namely, those of the triphenylmethane series and the azo-dyes, are compared with those of closely-related coloured substances, including the salts of the polynitrotriphenylmethanes (preceding abstract). It is shown that the original quinonoid formulæ given by E. and O. Fischer need only to be extended to conjugated-quinonoid structures to explain the optical properties, new schemes like those of Baker (*T.*, 1907, 91, 1490) being unnecessary.

In the case of the quinonoid salts of aminotriphenylmethanes, as in the case of the quinonoid alkali salts of nitrotriphenylmethanes, the maximum optical effect, that is, the typical colour, is already reached when there are two salt-forming groups in the molecule. A third amino-group actually has, if anything, a hypsochromic effect. A hydroxyl or methoxyl group in the place of a third amino-group has about half the optical effect; for example, hydroxy- and methoxy-malachite-greens are midway between malachite-green and crystal violet. Tetramethyldiaminorosaniline gives solutions of many colours, from bluish-red to yellow, in indifferent media, but they all give absorption curves like that of magenta, only more or less displaced.

The magenta dyes also closely resemble the reddish-violet salts of the aminoazobenzenes, and the three classes are, therefore, characterised by two components: (1) a quinonoid salt complex (*ac*-nitro-salt or ammonium salt) as chromophore, and (2) another group (nitro- or amino-) which forms a powerful auxochrome in conjugation with the quinonoid group, thus:



The effect of an acid on compounds of the last types is obviously to break the conjugation and so destroy the auxochrome.

Two new compounds are described. *Dimethoxydimethylaminotriphenylcarbinol*, $(\text{OMe}\cdot\text{C}_6\text{H}_4)_2\text{C}(\text{OH})\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$, bundles of very pale green crystals, m. p. 112° , is obtained by heating together dianisyl ketone, dimethylaniline, and a mixture of phosphorus pentoxide and oxy-chlorides, and is converted into *dimethoxyfuchsondimethyl-imonium chloride*, $(\text{OMe}\cdot\text{C}_6\text{H}_4)_2\text{C}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2\text{Cl}$, by means of hydrochloric acid. This dye has the typical appearance of cantharides, but it is not fast to light or washing.

Several sets of curves are reproduced in the original, but the lengthy discussion is largely polemical. J. C. W.

Relationship between Mechanical and Chemical Rotation and the Structure of Liquid Crystals. O. LEHMANN (*Ann. Physik*, 1919, [iv], **58**, 631—656).—A continuation of previously published work (*ibid.*, 1916, **51**, 353). The effects produced when the containing walls which hold liquid crystals are twisted whilst polarised light is passing through the crystals are investigated. The effects are examined by means of crossed nicols for *p*-azoxyphenetole and for the same substance to which colophony and cholesteryl benzoate have been added. Numerous diagrams of the appearance under the nicols are given. J. F. S.

The Rotation Dispersion of Butyl, Heptyl, and Octyl Tartrates. PERCY FARADAY FRANKLAND and FREDERIC HORACE GARNER (*T.*, 1919, **115**, 636—661).

Evolution of Very Dilute Solutions of Tetrachloroplatinic Acid in Complete Darkness and at Different Temperatures. MARCEL BOLL (*Compt. rend.*, 1919, **168**, 1108—1111).—A comparison of the changes and their velocities taking place in a very dilute solution of tetrachloroplatinic acid in the dark at temperatures between 10° and 100° , and those taking place in the light (compare A., 1912, ii, 407). The thermal acceleration is practically the same whether the action takes place in the dark or under the influence of high-frequency rays. W. G.

Collision of α -Particles with Light Atoms. I. Hydrogen. SIR E. RUTHERFORD (*Phil. Mag.*, 1919, [vi], **37**, 537—561. Compare E. Marsden, A., 1914, ii, 407; Marsden and Lantsberry, *Phil. Mag.*, 1915, [vi], **30**, 240).—"H"-particles, derived by passing α -particles through hydrogen, from "head-on" collisions between the α -particles and the nuclei of the hydrogen atoms, are also obtained, without using hydrogen, from thin-walled glass and quartz tubes filled with radium emanation, and from a deposit of radium-C on a nickel plate—from the latter more than the former. Special experiments showed that radium-C is not different in this respect from radium-A and the emanation, and these have also shown that oxygen and nitrogen atoms (see succeeding papers) can be put in

swift motion by collision with α -particles to cause scintillations outside the range of the α -particles, to which, probably, a large number of the scintillations, ascribed by Marsden to H-particles, were due. The homogeneous α -rays of radium-C deposited on a metal disk were exclusively used. The disk was washed with alcohol and heated in an exhausted tube to 300° for a minute to reduce "volatilisation" of the radium-C (Ratner). The H-particles were counted by the scintillations on zinc sulphide screens, and were similar to those produced by α -particles 3 mm. from the end of their range. The active disk was mounted in a tube capable of exhaustion, or of being filled with the gas studied, at a variable distance from an opening in the end covered with thin sheets of silver, aluminium, or iron of stopping power equivalent to from 4 to 6 cm. of air, the zinc sulphide screen being just outside the apparatus. The number of H-particles is ordinarily less than one in one hundred thousand of the α -particles, and can only be detected after the latter have been absorbed. β -Rays were suppressed by a strong magnetic field. The number of H-particles without any gas in the vessel was first determined. These are small in number relatively to those produced when the apparatus is filled with hydrogen, and it cannot be decided whether they originate from the radio-element itself or from hydrogen occluded by the materials in which it is contained. The number fell off, when metal screens were interposed, rapidly between the equivalent of 7 and 12 cm. of air, and then more slowly, a few being observed up to the equivalent of 28 cm. The metal screens—silver and aluminium—were heated to drive off occluded gases. Gold was found to be very free from hydrogen, but could not be used close to the zinc sulphide screen on account of the marked luminosity it produces on the screen beyond the range of α -particles, an effect that is being investigated.

The number of H-particles produced in hydrogen gas and their distribution with velocity differed markedly from the results calculated from the simple theory by Darwin's formula. The apparatus being filled with hydrogen at atmospheric pressure, the number of H-atoms was counted when aluminium foils were interposed before the screen. There was no diminution between the equivalent of 9 and 19 cm. air absorption, and then a slow decrease in the number took place, followed by a rapid one near the end of the range. Theoretically, between 9 and 19 cm. the number should have been reduced to 28%. This is only marked when long-range α -particles are used. As the range of the α -particles is reduced, the theoretical curves are more and more nearly approached. The absorption curve for H-particles produced by long-range α -particles is similar to that of the α -particles themselves, showing that the hydrogen atoms are thrown forward all at practically the same velocity and in the same direction as the α -particle is travelling, or at least within 10° or 15° from it. The fraction of the number of α -particles which produce one H-particle per cm. of path in hydrogen at *N.T.P.* was found to be about 10^{-5} . At 10 cm.

(eq. air absorption), the total number produced is ten times, at 19 cm. thirty-one times, the number calculated from the simple theory (Darwin). On the average, each α -particle of 7 cm. range of radium-*C* produces an H-particle when the perpendicular distance of its path from the centre of the hydrogen atom is equal to or less than 2.4×10^{-13} cm., and the results point to the view that within 3.5×10^{-13} cm., the field of force between the colliding nuclei undergoes rapid changes in magnitude, and probably direction. Since only one in 10^5 α -particles passing through 1 cm. of hydrogen produces an H-particle, and in this distance each α -particle passes through 10^4 hydrogen molecules, only one out of every 10^9 collisions produces an H-particle capable of being detected beyond the range of the α -rays. The helium nucleus, or α -particle, is pictured as a charged disk of radius about 3.6×10^{-13} cm., with its plane perpendicular to its direction of motion, and probably composed of four hydrogen nuclei and two nuclear electrons. This is regarded as being probably much deformed during close collisions. It is to be expected that it would break up, but no evidence of this has yet been observed.

F. S.

Collision of α -Particles with Light Atoms. II. Velocity of the Hydrogen Atom. Sir E. RUTHERFORD (*Phil. Mag.*, 1919, [vi], 37, 562—571).—The assumption in the preceding paper that the long-range scintillations observed in hydrogen are due to hydrogen atoms set in swift motion by their collision with α -particles is supported by their range, which agrees with that calculated for such H-particles by Darwin from Bohr's theory. The mass, charge, and velocity of these H-particles have been determined by measurements of the deflection they undergo in electromagnetic and electrostatic fields. As source of hydrogen, a film of paraffin wax 30 μ in thickness exposed to intense α -rays was used. The H-particles were passed through two slits and received on an external zinc sulphide screen, after passing through a sheet of iron, closing the end of the apparatus, equivalent in stopping power to 4 cm. of air. With the apparatus exhausted, the deviation in a magnetic field of the α -particles themselves was first found. The paraffin film and aluminium screens, equal in total stopping power, with the iron sheet, to 14.4 cm. of air, were then interposed, and the deflection of the H-particles found to be 1.45 times that of the α -particles of radium-*C*. This gives for mu_0/e , the product of the mass and initial velocity of the fastest H-particles divided by the charge, 3.15×10^5 . From theory, v_0 should be 1.6 v_0 , that is, 1.6 times that of the α -particles, and mu_0/e 3.2×10^5 . All the H-particles carried a positive charge, and no sign of negatively charged particles was observed. The electrostatic deviation between two parallel plates 6 cm. long and 1.55 mm. apart charged to 4500 volts was insufficient to deviate the H-particles completely, and it was calculated that 30,000 volts would be required. So the deflexion with a magnetic field was compared with that produced by a combined electrostatic and electromagnetic field acting in unison, and it was

found that a magnetic field of 238 gauss on the average was equivalent to an electric field of 1000 volts. This gives for u_0 the maximum velocity of the H-particle, 3.12×10^9 cm. per second. The calculated value, $1.6 u_0$, is 3.07×10^9 cm. per second. The value of e/m , consequently, is 10^4 e. m. units, which agrees very well with the value, 9570, for the H-ion in the electrolysis of water. This proves that for close collisions the conservation of momentum and energy holds good, and that there is no sensible loss of energy due to radiation.

The energy communicated to the H-particle is 0.64 that of the α -particle, and, after traversing the equivalent of 12 cm. of air, is 0.44, corresponding with that of an α -particle of range 2 cm. of air. The brightness of the scintillation it produces is, at all ranges, much less than is to be expected, and corresponds, for example, with that of an α -particle of range 0.5 cm. instead of 2 cm. This may be due to the energy spent per unit of path by an H-particle being only about one-sixth of that by an α -particle. A large proportion of instantaneous double scintillations was observed, and it was found, in comparison with α -particles, that the number was nearly double what is to be expected from probability considerations. It could not be settled, however, whether this effect is real or due to the eye being unable to distinguish separately the weak scintillations due to H-particles as readily as those produced by α -particles.

F. S.

Collisions of α -Particles with Light Atoms. III. Nitrogen and Oxygen Atoms. Sir E. RUTHERFORD (*Phil. Mag.*, 1919, [vi], 37, 571—580).—From Bohr's general theory of the absorption of charged atoms in passage through matter, which is substantiated experimentally for the α -particles and H-particles, the range x in hydrogen of an atom of charge e and mass m moving with a speed equal to that of an α -particle of range R is given by $x/R = mE^2/Me^2$, M and E being the mass and charge of the α -particle. For light atoms, with unit charge $x = mR$. Tables are given for x/R for singly charged atoms from hydrogen to gold travelling with a velocity calculated to be produced by impact of the atom in a "head-on" collision with the α -particle. For α -particles of range 7 cm., the maximum ranges in cm. to be expected are as follow: He 28, Li 19.6, Gl 15.4, B 12.4, C 11.2, N 9.3, O 7.8. Experiments with helium have shown that, if any long-range particles are produced, the number is very small compared with that produced in hydrogen, and it is concluded that the helium atoms carry a double charge and have the same range as the α -particles. Neither were any certain indications of long-range particles obtained for salts of lithium, glucinum and boron. Such experiments are much easier for gases, and in air numerous bright scintillations are observed for distances 2 cm. beyond the range of the α -particles. With a total absorption equivalent to 7.5 cm. of air, these "N-particles" and "O-particles" give scintillations equal in brightness to an α -particle of range about 1 cm. The scintilla-

tions for oxygen and carbon dioxide were of about the same range and brightness as those in air, but they were shown to arise in the gases, and not to be emitted from the radio-element itself. No evidence of singly charged carbon atoms from carbon dioxide was obtained. Estimating the relative numbers of high-speed particles in hydrogen, oxygen, and nitrogen, it was found that the numbers for the different gases are not very different. The long-range rays of range 11.3 cm. found by Rutherford and Wood in the active deposit of thorium (A., 1916, ii, 282) are such as would result from oxygen atoms present in the mica screens used, but the number—1 to 10,000 α -particles—was much greater than is to be expected from the experiments with radium-C, and further experiments are in progress.

F. S.

Collisions of α -Particles with Light Atoms. IV. An Anomalous Effect in Nitrogen. Sir E. RUTHERFORD (*Phil. Mag.*, 1919, [vi], 37, 581—587).—A surprising effect was noticed in the study of the "natural" scintillations due to H-particles, which it is difficult to decide whether they are due to the action of α -particles on occluded hydrogen in the radioactive material or support, or are expelled in the disintegration itself. With the apparatus described in the first paper, exhausted and filled with dry oxygen or carbon dioxide respectively, the number of natural scintillations observed diminished in about the ratio to be expected from the stopping power of the gas column. In dried air, however, the number increased, and with a total absorption equivalent to about 19 cm. of air was twice as great as with the apparatus exhausted. All experiments were made at absorptions greater than the equivalent of 9 cm. of air to eliminate the O-particles and N-particles described in the last paper. The additional H-particles were not due to moisture or dust nuclei and were observed in chemically prepared nitrogen, from ammonium nitrate, to an extent 1.25 times that observed for air. They were shown to arise from the volume of the gas, and were not due to a surface effect in the radioactive source. The H-particles so obtained from nitrogen had a somewhat greater penetrating power than those from hydrogen, but none could be detected beyond a range of 28 cm., and probably the difference is due to their being projected more in the line of flight of the α -particles than those resulting from hydrogen gas. The number from nitrogen at atmospheric pressure is equal to the number given in hydrogen at 6 cm. pressure, so that only one H-particle is given in nitrogen for every twelve collisions giving rise to N-particles. As regards both the brightness of the scintillations and the range, these long-range particles closely resemble, and in all probability are, H-particles, but to settle the point definitely it will be necessary to determine their deflexion in a magnetic field. Preliminary experiments indicate a similar deflexion, but to decide the question definitely it will probably be

necessary to employ a solid nitrogen compound free from hydrogen, and to discriminate between H-particles and possible particles of atomic mass 2.

If they are H-particles, it must be concluded that the nitrogen atom has been disintegrated during the close collision with an α -particle, and that the hydrogen nucleus is a constituent part of the nitrogen nucleus. This may account for the ranges of the N-particle and O-particle being the same, instead of differing by some 19%, as is to be expected. For if hydrogen is disrupted from the nitrogen atom, the energy of the impact would be shared between the two systems. Nitrogen is the only light atom of atomic mass $4n+2$, where n is a whole number, and its nucleus should consist of three helium nuclei and ten hydrogen nuclei. The latter may be outsiders of the main system of mass 12, and the close collision with an α -particle seems to be the most likely agency to promote the disruption of such a nucleus. It is not to be expected, a priori, that the velocity or range of H-particles, so produced from the nitrogen atom, should be identical with that of those produced by collisions in free hydrogen. F. S.

Precision-measurements in the X-ray Spectra. MANNE SIEGBAHN (*Phil. Mag.*, 1919, [vi], **37**, 601—612).—By a new method of measurement, the accuracy of wave-length measurements for X-rays has been increased a hundred-fold. The angle of the reflected rays is determined as the angle through which the same photographic plate has to be turned in order to receive impressions of the n th order reflection on both sides of the direct ray, the angles being read off an accurate circle scale. If ϕ is the angle of reflexion, and the plate is turned accurately 4ϕ (and the crystal nearly $2\phi+180^\circ$), the spectral lines on both sides would cover one another. In practice, the plate is turned nearly 4ϕ , and by measuring the distance between the lines, the small correction to exactly 4ϕ can readily be applied.

The plate and slit must have the same distance from the rotating axis of the reflecting face of the crystal and of the plate-holder, and during exposure the crystal may, if necessary, be continually turned through a small range, and for bad crystals irregularities so eliminated. Drawings of a spectrograph for vacuum built on this principle are given, and also for the X-ray tube found most suitable.

The wave-length of $\text{CuK}\alpha$ (the α -line of the K-series of copper) was determined to be $1537.358(\pm 0.033) \times 10^{-11}$ cm., when the lattice constant, d , of rock-salt is taken as 2.81400×10^{-8} cm., and of calcite 3.02904×10^{-8} cm. The relation of these two constants was accurately determined for $\text{CuK}\alpha$, $\text{FeK}\alpha$, and $\text{SnL}\alpha$, the wave-lengths found for the last two lines being 1932.39 and 3592.94 respectively. The lattice constant found for potassium ferrocyanide was 8.408×10^{-8} , instead of the value 8.454 used by Moseley, and

the latter's wave-length tables must be diminished by 0.54% in consequence. The following table of wave-lengths is given:

Element.	Atomic number.	$\lambda \cdot 10^{-11} \text{ cm.}$	
		$K\alpha_1$.	$K\beta_1$.
Chlorine	17	4718.70	—
Potassium	19	3733.86	3447.37
Calcium	20	3351.86	3087.89
Scandium	21	3025.26	2774.54
Chromium	24	2285.17	2081.44
Iron	26	1932.39	1753.97
Cobalt	27	1785.24	1617.58
Nickel	28	1654.67	—
Copper	29	1537.36	1389.53

This great increase of experimental accuracy is employed to test the formulæ of Sommerfeld for the difference of wave-length between the α_1 and α_2 doublet of copper in the K -series with the result, $0.373(\pm 0.005) \times 10^{-8}$, in complete agreement with theory. Preliminary measurements of the wave-length difference of the β - and β' -lines of iron, manganese, and chromium give 3.55, 4.55, and 4.87 ($\times 10^{-11} \text{ cm.}$) respectively. The formulæ of the $K\alpha$ -series given by Moseley, Sommerfeld, Debye, and J. Kroo are compared with the experimental values given in the above table, with results decidedly in favour of the formula of the last-named, the difference between the calculated and experimental results varying regularly from -0.2% for chlorine to +0.017% for copper. F. S.

Ionisation by Canal Rays. J. STARK (*Jahrb. Radioaktiv. Elektronik*, 1918, **15**, 329—364).—A summary of the literature of the subject with a bibliography. The account is divided into three chapters: (1) emission of electrons from metallic surfaces; (2) emission of electrons from gases; (3) emission of positive ions by canal rays. E. H. R.

The Theory of Electrolytic Ions. X. The Conductivity of Multi-valent and Multi-stage Electrolytes. RICHARD LORENZ (*Zeitsch. anorg. Chem.*, 1919, **106**, 49—75).—A theoretical paper in which the general theory of electrical conductivity is discussed from the viewpoint of Planck's conductivity equation. It is pointed out that the conventional use of normal solutions and equivalent conductivities leads to much confusion. It is better to refer all measurements to molecular quantities, no assumption being then made as to the manner in which the electrolyte dissociates. The degree of dissociation is independent of the manner in which it takes place, and is simply defined as the ratio of the number of altered molecules to the number originally present. The molecular conductivity quotient μ/μ_∞ has been deduced from Planck's equation for a number of different, typical kinds of ionic dissociation. This quotient is identical with the degree of dissociation only in the case of single-stage electrolytes, that is, of those which dissociate in one stage, whatever be the number of different

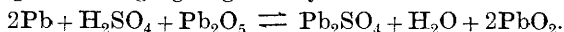
ions formed. In the case of multi-stage dissociation, the conductivity quotient bears no relation to the degree of dissociation and is generally smaller than this. E. H. R.

Cause of the Small Electrical Conductivity of Non-aqueous Salt Solutions. R. BEUTNER (*Zeitsch. Elektrochem.*, 1919, 25, 97—100).—From a series of electrical conductivity measurements of solutions of salicylic acid and dimethyltoluidine in nitrobenzene solution, the author asserts that the cause of the slight conductivity of solutions of salts in non-aqueous solutions is a non-electrolytic dissociation which opposes the electrolytic dissociation. This is supported by the observations that a solution of an acid or a base in a non-aqueous solvent has a very slight conductivity, whilst a similar solution of acid and base has a very much larger conductivity. The conductivity of a solution of acid and base changes regularly when the concentration of the acid is changed, the base being kept constant and vice versa. Further, the molecular conductivity decreases with increasing dilution. It is stated that the above observations are in keeping with the assumption that in most non-aqueous solvents an equilibrium $\text{salt} \rightleftharpoons \text{acid} + \text{base}$ exists, so that both free acid and base exist side by side with the salt. Hence the salt, as such, has a considerable conductivity, whilst the acid and base alone have practically none. J. F. S.

Contra-electromotive Force of Polarisation in Sulphuric Acid. ALBERT NOYES (*Compt. rend.*, 1919, 168, 1049—1052).—The contra-electromotive force of sulphuric acid at 20° is 1.68 volts, and diminishes at first inversely as the absolute temperature. Between 60° and 120°, it diminishes more rapidly, and above the latter temperature remains practically constant. This may be attributed to a difference in the mode of ionisation, which is at first into $\text{H}^+ \text{HSO}_4^-$ and then 2H^+ and SO_4^{2-} . W. G.

The Potential of a Nitrogen Electrode. FRANCIS LAWRY USHER and RAMAVENKABASUBBIER VENKATESWARAN (*T.*, 1919, 115, 613—618).

The Chemical Process of the Lead Accumulator. CH. FÈRY (*Bull. Soc. chim.*, 1919, [iv], 25, 223—234).—The author considers that the theory of "double sulphating" is incorrect, and that the behaviour of the lead accumulator is similar to that of a primary cell with a solid depolariser, with the difference that the negative electrode gives rise to an insoluble salt. The reaction during normal discharging and charging is given by the reversible reaction:



The subsulphate is a black powder and, unlike the normal sulphate, has a certain conductivity. The higher oxide, the active material of the positive electrode, is a black, endothermic substance and a powerful oxidising agent. W. G.

Relationship between Electrolysis and Photolysis and Electrolytic Non-reversibility. EMIL BAUR (*Zeitsch. Elektrochem.*, 1919, **25**, 102—109).—The author regards photolysis as analogous to a type of electrolysis. If a substance E absorbs a light quantum it becomes polarised and a potential difference is set up.

This is symbolically expressed by the equation $E + h\nu = E^{\oplus}_{\ominus}$. This conception of photolysis is compared with electrolytic action, and it is shown that the electrolysis of sodium acetate and the photolysis of acetic acid yield the same products and respectively are to be expressed by similar equations, thus: $2\text{CH}_3\cdot\text{COO}' + 2F = \text{C}_2\text{H}_6 + 2\text{CO}_2$; $\text{U}^{\text{VI}} \left\{ \begin{array}{l} \oplus\oplus + 2\text{CH}_3\cdot\text{COO}' \\ \ominus\ominus + \text{U}^{\text{VI}} \end{array} \right. = \text{C}_2\text{H}_6 + \text{U}^{\text{IV}} + 2\text{CO}_2$. Glycollic acid in the presence of oxidising agents, such as ferric salts, cupric salts, or uranyl salts is converted into formaldehyde under the influence of light, and it is experimentally shown that electrolysis gives the same product. Oxalic acid is converted by light in the presence of uranyl salts into carbon monoxide and carbon dioxide, but it was found impossible to detect carbon monoxide in the products of electrolysis of oxalic acid. In the light of the present theory the author re-states with modifications the theory recently (A., 1913, i, 443) advanced with regard to the initial stages of the assimilation of carbon dioxide by plants.

J. F. S.

Disgregation of the Oxidation Products Produced on Silver Anodes in Alkaline Media. FR. JIRSA (*Zeitsch. Elektrochem.*, 1919, **25**, 146—151).—A silver anode which has been polarised in alkaline solution by direct current is temporarily depolarised by telluric acid, whilst alternating current with simultaneous polarisation by direct current makes an over-voltage on the anode impossible and depolarises permanently. When a silver anode in an alkali hydroxide is polarised by alternating current alone, it is oxidised, the current being effective only as far as its anodic component is concerned. The oxidation product, produced when an alkali hydroxide is electrolysed between silver electrodes, disperses itself throughout the solution as a colloidal suspension. When direct current is employed the suspension is Ag_2O_2 , but if the solution of alkali contains telluric acid the suspension produced consists of Ag_2O_3 ; with alternating current the oxide Ag_2O is produced.

J. F. S.

Size of Particle, Solution Tension, and Sintering. E. PODSZUS (*Zeitsch. Elektrochem.*, 1919, **25**, 100—101).—A theoretical paper, in which a paper by Kohlschütter and Vuilleumier (this vol., ii, 9) is criticised.

J. F. S.

An Explanation of Space-filling Numbers. RICHARD LORENZ (*Zeitsch. anorg. Chem.*, 1919, **106**, 46—48).—It has been shown (this vol., ii, 212) that, for a number of univalent inorganic cations, the space-filling number ψ increases regularly with the number of

atoms in the ion. The space-filling number is a ratio of two volumes, that is, of the absolute volume of the ion, ϕ , to the ionic volume V_0 calculated additively from the usual atomic volumes of the constituent atoms. Since then the ratio increases as the number of atoms increases, it follows that ϕ increases at a greater rate than V_0 , that is to say, ϕ increases more rapidly than it would do if it were an additive quantity. This can only be explained on the assumption that, when the atoms combine, a certain amount of interstitial space is included in the molecule, with the result that the ratio of the absolute volume of the molecule to the volume of its "sphere of influence" gradually increases as the molecule becomes more complex.

E. H. R.

Deduction of Cryoscopy from the General Laws of Solubility. ALBERT COLSON (*Compt. rend.*, 1919, 168, 1047—1049).—A mathematical discussion, in which the author, starting with his law of solubility, deduces Raoult's law.

W. G.

High Temperature Researches. XII. The Measurement of Vapour Tensions at Very High Temperatures with some Observations on the Solubility of Carbon in Metals. OTTO RUFF and BERNHARD BERGDahl (*Zeitsch. anorg. Chem.*, 1919, 106, 76—94).—A new method has been devised for measuring the vapour pressures of metals at high temperatures and for the determination of their boiling points. The method consists in observing the gradual loss of weight occurring whilst the metal is exposed to a gradual, uniform rise of temperature to beyond its boiling point. The loss of weight is plotted against the temperature, and from the curve so obtained the boiling point is estimated. Before the boiling point is reached the curve is approximately logarithmic, and beyond this point becomes linear, but the change at the boiling point is not as sharp as might be expected. For the determinations, a small quantity of the metal, about 0.5 gram, is heated in a very small crucible of quartz or carbon. The crucible is suspended from a specially designed spring balance, by which the loss of weight is observed, and hangs inside a resistance furnace which can be evacuated and filled with an indifferent gas at any desired pressure, which is recorded by a manometer. Special provision is made to ensure a uniform rate of rise of temperature. The following results are recorded for the boiling points: mercury, 357°; cadmium, 785°; zinc, 930°; arsenic, 568°; antimony, 1330°; bismuth, 1490°; lead, 1555°; tin, 2270°; copper, 2305°; silver, 1950°; gold, 2600°. The results are compared with those of other observers, and in the cases of mercury, zinc, and cadmium, for which metals the older measurements are considered to be fairly trustworthy, the agreement is very satisfactory. The results for the vapour pressure of mercury agree well with those of Ramsay and Young (*T.*, 1886, 49, 453) at temperatures near the boiling point, but at lower temperatures the divergence is considerable. The new method appears to be more accurate near the boiling point.

When the measurements were made in carbon crucibles, the metal became saturated with carbon, and it was possible to estimate the solubility of carbon in the metals antimony, bismuth, lead, tin, copper, silver, and gold. In all cases the solubility was found to be too low to influence the boiling-point determinations. The solubility is highest in lead (0.094% at 1555°) and antimony (0.094% at 1327°), and in the other metals little more than a trace of carbon is dissolved.

E. H. R.

Vapour Tensions of the Metals. J. W. RICHARDS (*J. Franklin Inst.*, 1919, **187**, 581—598).—A theoretical discussion on the vapour pressures of liquid and solid metals in connexion with Trouton's rule and Richards' rule. The many equations for expressing vapour pressure as a function of the temperature are discussed. Tables are given of vapour pressures and the latent heats of vaporisation of some forty-three elements, in the former case for the solid at 0° and at the melting point; and the equations for calculating the vapour pressure at any temperature are given for both the solid and liquid. The practical significance of the vapour pressure is indicated in (i) the distillation of metals (Parkes', desilverisation process), (ii) loss of zinc in brass melting, (iii) loss of metal as fumes, (iv) sherardising and calorising, and (v) vapour losses during electrolysis.

J. F. S.

A New Laboratory Fractionating Column and the Measure of its Efficiency. M. H. ROBERT (*Compt. rend.*, 1919, **168**, 998—1001).—The column is really a double one. The lower column is an ordinary bulb fractionating column with beads, but it is surrounded by a glass vacuum jacket, which is highly evacuated. Above this column and sealed on to it is another simple fractionating column, surrounded by an outer jacket through which air is caused to circulate, and on top of this is the still-head. The column gave very satisfactory results with mixtures of alcohol and water, acetic anhydride and acetic acid, benzene and toluene, in the extraction of hexahydrotoluene from essence of Borneo, and in the fractionation of light petroleum. Using the formula $E = (a - b)/v$, and applying it to the benzene-toluene mixture, where v is the amount of benzene in the original mixture and a and b are the amounts of benzene and toluene in the first half of the distillate, the efficiency of the column was found to be 0.94 as against 0.73 for a Vigreux column and 1.0 for a perfect column.

W. G.

Direct Determination of the Temperature Exponent in the Equation of State of Fluids. É. ARIÈS (*Compt. rend.*, 1919, **168**, 930—933).—Knowing the values of T_c , P_c , and of the vapour pressures as well as the volumes v_1 and v_2 at a given temperature, the author has determined the value of n in the equation $(v_1 - v_2) = RT_c x (\gamma_1 - \gamma_2) / 8P_c \sigma^{n+1}$, for each of the seven substances for which the formula was obtained (compare this vol., ii, 184). The accuracy of these determinations has been tested by calculating the

variations of $(v_1 - v_2)$ with temperature and comparing the results against those observed by Young. The agreement is good. The values obtained for n increase by 0.04 for each increase of three atoms in the molecule of the substance, and there is an indication that the value of n for diatomic and triatomic substances must be close to but just greater than unity, that is, between 1 and 1.06.

W. G.

The Theory of the Gasification Process. [Producer Gas.] WA. OSTWALD (*Chem. Zeit.*, 1919, **43**, 229—231).—Three fundamental thermo-chemical equations represent the changes occurring in a gas producer: (1) $C + O_2 = CO_2 + 97.6$; (2) $C + 2H_2O = CO_2 + 2H_2 - 18.8$; (3) $C + CO_2 = 2CO - 38.8$. If the carbon is utilised in these three changes in the relative proportions a , b , and c respectively, the complete process may be represented by the equation $(a + b + c)C + aO_2 + 2bH_2O = (a + b - c)CO_2 + 2bH_2 + 2cCO + 97.6a - 18.8b - 38.8c$. Only two of the quantities a , b , and c are independent variables, and any desired values are readily represented by means of triangular co-ordinates after the manner introduced by Gibbs. Any point in the diagram may be represented by the equation as above. The values of a , b , and c can readily be determined from an analysis of the gas produced. The area of the triangle of reference is divided into two regions: (1) a region of combustion and gasification, and (2) a region of gas regeneration. Illustrations are given of the respective situations in these regions of the various technical gas mixtures. The author shows how isothermals or isocalorics are to be diagrammatically represented, and how an isocaloric solid may be constructed in any given case. The diagrams enable the thermo-chemical and volumetric characteristics of the process under any given circumstances to be readily ascertained, and to determine the effect of alteration of working on the course of the reactions, the coal consumed, the heating value of the gas obtained, etc.

J. S. G. T.

Critical Temperatures of Solution in Aniline of the Principal Hydrocarbons occurring in Light Petroleum.

G. CHAVANNE and L. J. SIMON (*Compt. rend.*, 1919, **168**, 1111—1114).—The temperature measured was in each case that above which the mixture of aniline and hydrocarbon was homogeneous, no matter what its composition. The hydrocarbons examined were those occurring in light petroleum, b. p. below 150°. The straight chain aliphatic hydrocarbons had practically the same critical temperature of solution, 71°, regardless of their molecular weight. Similarly, the β -methyl hydrocarbons all had a critical temperature of solution of about 74°. The cyclic hydrocarbons, cyclohexane, etc., had critical temperatures very much lower than those of the corresponding straight chain hydrocarbons, and again the substitution of a methyl group had a marked effect. For isomeric hydrocarbons, the critical temperatures and the densities varied in an inverse ratio.

W. G.

Density and Temperature. W. HERZ (*Zeitsch. Elektrochem.*, 1919, **25**, 145--146).—A theoretical paper in which the change of density in homologous series with temperature change is considered. It is shown that whilst the density of the members of homologous series at low and medium temperatures can show both a rising and a falling density with increasing number of carbon atoms, at high temperatures, near the critical point, the density increases regularly with increasing number of carbon atoms. The ratio of the densities of two members of an homologous series increases regularly with increasing temperature. J. F. S.

Regularities in the Magnitudes of Molecular Volumes. FRITZ EPHRAIM and EDUARD MICHEL (*Helv. Chim. Acta*, 1919, **2**, 266--276).—A further discussion on molecular volumes and the percentage contraction on the sum of the constituent atomic volumes (compare A., 1917, ii, 535). Tables are given showing the percentage contraction, calculated according to the equation $c = \text{mol. vol.} \times 100 / \Sigma \text{ at. vol.}$, for compounds of the alkali metals with most of the atoms or radicles, F, Cl, Br, I, O, OH, SO₄, SeO₄, NO₃, ClO₃, ClO₄, IO₃, IO₄, MnO₄, the necessary data and the authorities being quoted in another summary. Comparing the compounds with a fixed negative part, the percentage contractions are very similar, the caesium haloids exhibiting the only abnormally great contractions. Comparing the various salts of one metal, however, great variations appear, fluorides showing contractions of about 62% and iodides about 30%. In spite of the uncertainty of much of the data, sufficient regularities are revealed to make it worth while to pursue such a line of inquiry further. J. C. W.

Standard Substances for the Calibration of Viscometers. E. C. BINGHAM and R. F. JACKSON (*Bull. Bureau of Standards, U.S.A.*, 1918, **14**, [1], 59--86).—As liquids of greater viscosity than water, solutions of sucrose and mixtures of ethyl alcohol and water are suitable and convenient for use in calibrating viscometers. The viscosities of ethyl alcohol-water mixtures have been determined by several observers, with fairly concordant results, but the accuracy of existing data relating to sucrose solutions has been questioned. In the present work, the viscosities of 20% and 40% solutions of sucrose (by weight) were determined at temperatures from 0° to 100°, and that of a 60% solution from 10° to 95°, with results generally somewhat higher than those obtained hitherto. Existing data relating to the viscosity of water were also reviewed and corrected, the viscosity and fluidity being calculated for every degree from 0° to 100°. In discussing the relative merits of absolute and specific units for expressing viscosity, the centipoise (cp., the one-hundredth part of the *C.G.S.* unit) is favourably considered. By the use of this unit, the absolute and specific viscosities of a liquid are practically the same, provided that water at 20° be taken as the standard. The most probable value for the viscosity of water at 20° was found to be 1.005 cp.

W. E. F. P.

Occlusion of Hydrogen by the Metallic Elements and its Relation to Magnetic Properties. DONALD P. SMITH (*J. Physical Chem.*, 1919, **23**, 186—202).—A theoretical paper in which the literature on the occlusion of hydrogen by metals is discussed. It is shown that the alloys produced when hydrogen is occluded by metals are to be sharply distinguished from other types of binary hydrogen compounds (KH , SbH_3), and that these and the hydrogen-occluding metals occupy definite sharply divided regions of Werner's periodic table. The power of occluding hydrogen is compared with the magnetic properties of the metals, and it is shown that elements with a specific magnetic susceptibility greater than 0.9×10^{-6} at the ordinary temperature occlude hydrogen strongly, whilst those with a smaller susceptibility do not occlude hydrogen. Possible exceptions to this generalisation are copper, rhodium, and thorium. Hence it is concluded that the capacity of a metal to occlude hydrogen in large amounts is restricted to those of strongly magnetic character. A fairly comprehensive bibliography of the occlusion of hydrogen by metals is appended to the paper. J. F. S.

The Surface Condensation (Adsorption) of Water-vapour and Gases and the Errors in Weighing arising Therefrom. K. SCHERINGA (*Pharm. Weekblad*, 1919, **56**, 94—107).—A review of the literature bearing on this subject. The author concludes that errors in weighing due to the true adsorption of water vapour or air on the surface of the most commonly occurring substances may be neglected. W. S. M.

Adsorption of Electrolytes by Charcoal. PETER RONA and LEONOR MICHAELIS (*Biochem. Zeitsch.*, 1919, **94**, 240—260).—All salts, acids, and alkalis are adsorbed by charcoal, the anions and cations being adsorbed in equivalent amounts. Iodides, cyanides, and aluminium trichloride showed a slight difference in the adsorption of anions and cations, which is apparently not due to the actual process of adsorption. The adsorbability of a salt is determined by that of its component ions. Anions are adsorbed in the order $\text{SO}_4 < \text{HPO}_4$, $\text{Cl} < \text{Br} < \text{NO}_3 < \text{I} < \text{CNS} < \text{OH}$, and cations in the order K , Na , $\text{NH}_4 < \text{Ca}$, $\text{Mg} < \text{Zn} < \text{Cu} < \text{Al} < \text{H}$. A strongly adsorbable ion will supersede one possessing a lower adsorbability. J. C. D.

Adsorption by Precipitates. I. HARRY B. WEISER and J. L. SHERRICK (*J. Physical Chem.*, 1919, **23**, 205—252).—The amount to which the following anions, chloride, bromide, iodide, chlorate, permanganate, nitrate, nitrite, cyanide, thiocyanate, ferrocyanide, and ferricyanide, are adsorbed by barium sulphate has been determined. Barium sulphate was precipitated by mixing a solution of sodium sulphate with solutions of barium salts of the various acids yielding the above-named anions, and the precipitate analysed. One hundred gram-mols. of barium sulphate adsorb

0.056 equiv. ions, I' ; 0.220, CNS' ; 0.310, CN' ; 0.831, Br' ; 1.760, Cl' ; 2.695, $Fe(CN)_6^{III}$; 2.847, MnO_4' ; 5.837, ClO_3' ; 7.467, NO_3' ; 8.482, NO_3' ; 13.201, $Fe(CN)_6^{IV}$. In the case of the chlorate and permanganate ions, the adsorption is less when an excess of sodium sulphate is used in the precipitation. Changes in the conditions of precipitation affect the amount of adsorption, but not the order in which the ions are adsorbed. The observed order is not in accord with Schulze's law, although the quadrivalent ferrocyanide ion is most strongly adsorbed; but there are four univalent ions more strongly adsorbed than the tervalent ferricyanide ion, and there is a wide variation in the amounts of univalent ions adsorbed. Determination of the order of the ions by direct analysis of the adsorbing phase is preferable to deducing the order from coagulation data, since the former method is superior in accuracy. It is probably inaccurate in any case to assume that the ion with the same charge as the colloidal particles has no effect in determining the critical coagulation of the colloid by electrolytes. It is more probable that the relatively small effect of the ion with the same charge as the colloid may be lost sight of altogether, because of the errors inherent in the experimental method. The order of adsorption of anions by barium sulphate is the reverse of that deduced from Hofmeister's data (*Beitr. chem. Physiol.*, 1904, 5, 27) on the coagulation of albumin by electrolytes. The adsorption by charcoal and hydrated ferric oxide is more nearly what it is with barium sulphate. The adsorption for ions by a given adsorbent is controlled by the nature and valency of the ion. With ions of the same general character, the specific character of the adsorption is not very pronounced, and the valency factor predominates. Thus nitrate and nitrite ions are adsorbed to nearly the same extent, and among the cyanogen derivatives the order $Fe(CN)_6^{IV} > Fe(CN)_6^{III} > CN'$, CNS' is observed. Nitrates are adsorbed more than chlorates and chlorides, an observation in keeping with analytical practice. Colloidal solutions of barium sulphate are usually positive, due to strong preferential adsorption of barium ion.

J. F. S.

The Congo Dyes and Adsorption as the Preliminary Phase of Chemical Union. E. WEDEKIND and H. RHEINBOLDT (*Ber.*, 1919, 52, [B], 1013—1021. Compare Wedekind and Rheinboldt, A., 1914, ii, 626).—The behaviour of the blue solution obtained by treating Congo-red with acids towards various colloids has been examined; it is found that acid gels which are free from electrolytes (silicic acid, metastannic acid, titanin acid, tungstic acid, molybdic acid, vanadic acid) do not adsorb the Congo-dye acid and do not cause any change in colour on heating; basic gels, on the other hand (oxides of zirconium, thorium, aluminium, lanthanum, zinc, glucinum, iron, and chromium), adsorb the dye acid and when heated, assume the red colour which is characteristic of the salts. It appears probable that the Congo-acid belongs to the weakest class of acids, and that aqueous solutions of Congo-

red, in consequence of hydrolysis, always contain a greater or less amount of the red, azoid, free Congo-acid, which is transformed by hydrogen ions into the blue, insoluble isomeride. The adsorption of the Congo-acid is attributed to the formation of a primary adsorption compound of the free blue acid, which when warmed or preserved becomes converted (probably through the red acid) into a complex salt of acid and base. The phenomenon thus gives an experimental confirmation of the hypothesis that, particularly in heterogeneous systems, chemical action is preceded by the production of an adsorption compound.

Similar behaviour is observed with other dyes, such as benzo-purpurin 4B, benzopurpurin 10B, naphthalene-red, benzo-orange R, Congo-corinth G, and Congo-corinth B.

H. W.

Osmotic Pressures Derived from Vapour Pressure Measurements: Aqueous Solutions of Cane-sugar and Methyl Glucoside.

THE EARL OF BERKELEY, ERNALD G. J. HARTLEY, and C. V. BURTON (*Phil. Trans.*, 1919, [A], **218**, 295—349).—The compressibility of solutions of sucrose and α -methyl glucoside has been determined in a series of concentrations at the temperatures 0° and 30°. In general, the method and apparatus adopted is similar to that used in the case of calcium ferrocyanide (A., 1909, ii, 126). The glass containing tubes, previously used, are, however, replaced by metal tubes fitted with a number of plate-glass windows, and the piezometer is divided into two limbs, thus providing for more rapid temperature adjustment. The apparatus was tested with water and mercury, and for these substances the following results were obtained: mercury, at 0°, mean relative coefficient of compressibility between 1—101 atms., 0.169×10^{-5} ; at 1.8°, mean relative coefficient between 1—110 atms., 0.171×10^{-5} ; at 29.5°, mean relative coefficient between 8—150 atms., 0.165×10^{-5} . Water at 0.12°, absolute coefficient of compressibility between 17—48 atms., 5.085×10^{-5} ; at 30.01°, absolute coefficient between 17—48 atms., 4.458×10^{-5} . In the case of sucrose at 0°, compressibility coefficients were obtained ranging from 4.391×10^{-5} for a solution containing 180 grams of sucrose per litre over the pressure range 0—20 atms., to 2.235×10^{-5} for a solution of 215.4 grams of sucrose in 100 grams of water over the pressure range 10—27 atms. At 30°, values were obtained varying from 3.335×10^{-5} for a solution of 420 grams of sucrose per litre over the pressure range 0—27 atms. to 2.205×10^{-5} for a solution of 243 grams of sucrose in 100 grams of water over the pressure range 88—116 atms. In the case of α -methyl glucoside at 0°, a solution of 23 grams in 100 grams of water gave the coefficient 4.078×10^{-5} over the pressure range 17—48 atms., and a solution of 92 grams in 100 grams of water gave the coefficient 2.893 over the pressure range 0—44 atms. At 30°, for the same solutions, the values 3.848×10^{-5} over the range 20—31 atms. and 2.979×10^{-5} over the range 24—75 atms. were found respectively. Vapour-pressure determinations of solutions of sucrose, α -methyl glucoside,

and sulphuric acid have been made at 0° and 30° in an apparatus previously described (A., 1906, ii, 599). The possible sources of error in the method of determination are discussed at some length, and in the actual experiments these are avoided or corrected in the results. Very full tabulated results are given for the three substances measured, and from the results the osmotic pressure is calculated and compared with the experimentally determined value. The calculations are made by means of the expression

$$P = \log_e [l_0/l_1 - (l_0/l_1 - 1)\pi_0/B] \times RT/s,$$

where P is the osmotic pressure, s is the mean specific volume over the range $1 - (1 + P)$, l_1 and l_0 the loss of weight of the solution and solvent respectively, ρ_1 and ρ_0 the corresponding vapour densities, $\pi_{\pi'}$ and π_0 the corresponding vapour pressures, B the barometric pressure, $\pi_{\pi'}$ and π_0' the observed vapour pressures, and $[l_0/l_1 - (l_0/l_1 - 1)\pi_0/B] = \rho_0/\rho_1 = \pi_0'/\pi_{\pi'}$. The values previously published for calcium ferrocyanide (*loc. cit.*) are recalculated to allow for the "Burton correction," that the volume of the air entering the liquid is slightly different from that leaving it.

J. F. S.

The Experimental Investigation of Crystal Structure by means of X-Rays. R. GROSS (*Jahrb. Radioaktiv. Elektronik*, 1918, 15, 305—329).—A useful account is given of the methods which have been developed for investigating crystal structure by means of Röntgen rays. The methods described are the Bragg reflexion method, the Laue photographic method, and the Debye-Scherrer method, by means of which a crystalline powder can be examined in place of a well-developed crystal. The results which have been obtained by the last method are particularly important, as they show that substances formerly considered to be amorphous are in reality crystalline. Thus it was found that soot has essentially the same structure as graphite, and it becomes necessary to revise our opinions of the solid state. Probably there are no true amorphous solids, only crystals and liquids with varying degrees of viscosity up to the high viscosity of the glasses. E. H. R.

Kineto-electro-magnetic Theory of Crystals. J. BECKENKAMP (*Verh. Physik. Med. Ges. Würzburg*, 1918, 45, 135—163; from *Chem. Zentr.*, 1919, i, 273).—The previously described models of the constitution of the atom are reviewed and Bohr's theory is extended. The helium atom must consist of four positive nuclei which, by reason of mutual repulsion, occupy the corners of a regular tetrahedron. If each tetrahedron face contains the path of an electron, the four normals constitute magnetic axes which form an astatic system, that is, one in which no external magnetic action is exhibited at a distance. The atom itself is electrically neutralised. The lines connecting the centres of gravity of atoms united by valencies form polar electric axes. In a homogeneous regular crystal, the chemical molecules appear to be invariably arranged in a four-fold cubic lattice, the latter consisting of four

interlocked simple cubic lattices. In each of these, the electric axes of all molecules are directed towards similar tetrahedra normals. In homogeneous regular crystals, therefore, the electric axes of the chemical molecules form an astatic system. The crystalline metals, copper, silver, and gold, as well as lead and aluminium, have, accordingly, monoatomic molecules, crystalline carbon a diatomic molecule, since in the first cases the atoms are arranged in one, in the second instance in two, four-fold cubic lattices. According to this hypothesis, arsenic, antimony, bismuth, and tungsten have tetra-atomic molecules in the crystalline state. In other crystals, the astatic system may be built in two ways (two parallel and opposite axes or two axes intersecting at 120°), or in accordance with the four directions of the tetrahedra normals. This theory differs from that of Bohr, since the valency is regarded from a uniform principle, the astatic arrangement of the paths of the electron, and Bohr's axioms are deduced from general or electromagnetic laws.

H. W.

Recrystallisation in Metals. G. TAMMANN (*Nachr. K. Ges. Wiss. Göttingen*, 1918, 1—11; from *Chem. Zentr.*, 1919, i, 321—322. Compare A., 1918, ii, 447).—During the cold working of metallic castings, planes are developed in the crystallites in which the neighbouring portions of the crystallite displace one another. In this manner, a fluid structure is attained which greatly affects the properties of the casting, particularly with regard to elasticity. The original structure returns on heating, and also the original properties. The cause of recrystallisation lies in the formation of minute new crystallites in the débris of the crystallites of the cold-worked metal; these increase very slowly at the temperature of actual commencement of the process, but with increasing rapidity as the temperature rises. If the temperature is increased in steps, each increase is accompanied by enlargement of the granules, which speedily ceases, but recommences with each new rise in temperature. An attempt is made to explain the phenomena of recrystallisation on the following lines. Two crystals in contact can only be in equilibrium with one another when crystallographically-equivalent lattice planes of both crystals lie in one plane at the surface of contact; the two space lattices must either form a single lattice or the plane of contact must be a twin plane. The two lattices must occupy a definite position with respect to one another. If one or other of these conditions is not fulfilled, new net planes of intermediate orientation are formed at the plane of contact (that is, recrystallisation begins) as soon as the temperature is raised sufficiently for appreciable change in position of the atoms or molecules in the lattice to occur. Since it is highly improbable that the contact of two crystals will occur in such a manner that a net plane of each crystal lies in one plane, recrystallisation will almost always take place at the meeting point of two crystallites. Twin formation shows that the contact of two crystals in a common plane of symmetry does not disturb the equilibrium. In twin formation,

the plane is not formed by the accidental meeting of two growing crystals, but is due to the growth of each. Twin crystals may consequently be expected to be frequently formed during recrystallisation, but the degree will vary with different metals.

Recrystallisation commences with tin after half an hour's heating at 45°; at 150°, the new particles are still relatively small. Lead behaves very similarly. With zinc, recrystallisation is distinctly evidenced at 75° by the formation of relatively large crystallites; the size of the latter decreases with increase of temperature up to 250°, and then increases, slowly at first, more rapidly from 350°. The particles are smallest between 150° and 300°. For aluminium, the minimum occurs between 300° and 500°. Observations are also recorded on rolled copper and impure tin. The unusually marked dependence of the size of the particles after recrystallisation on the degree of deformation of iron is readily interpreted by the author's hypothesis.

H. W.

Eutexis and Dilute Solutions. ALB. COLSON (*Compt. rend.*, 1919, **168**, 942—944. Compare this vol., ii, 186).—Starting with the law of solubility (1), $425L = T(V + \epsilon)i \frac{dC}{dT}$, the volume V of the solvent, which contains 1 mol. of the solute in saturated solution, increases with cooling when $L > 0$. It attains a minimum when L changes sign. At the eutectic point, it reaches a maximum, where it remains constant, and at the same time T and C remain constant. In other words, the solution maintains a constant composition, which is the same as that of the solid deposited. If to such a solution at a temperature equal or inferior to the eutectic temperature T_e , some of the solvent in the solid state is added, it remains in that form until the temperature rises above T_e . The solubility of the solvent in the solution may be expressed by (2) $425L' = T(V' + \epsilon')i' \frac{dC'}{dT}$, and $\frac{dC'}{dT} = -\frac{dC}{dT}$. In other words, equation (1) gives the saturation of a substance A in a substance B , whilst equation (2) is relative to the saturation of B in A . The point of intersection of the two curves gives the eutectic point.

W. G.

Estimation of the Size and Internal Structure of Colloidal Particles by Means of Röntgen Rays. P. SCHERRER (*Nachr. Ges. Wiss. Göttingen*, 1918, 96—100; from *Chem. Zentr.*, 1919, i, 322—323).—The method of Debye and Scherrer (*Physikal. Zeitsch.*, 1916, **17**, 277) has been applied to the determination of the size and structure of typical organic and inorganic colloids. Two cases are possible, depending on the presence or absence of crystalline structure in the single colloid particle. In the former case, numerous interference figures are to be expected in the Röntgen photographs arranged in a manner characteristic of the space lattice. The position of the interference figures does not depend on the magnitude of the single crystals, but on its breadth. In the absence of crystalline structure, one or two very flat maxima in the region of the incident Röntgen ray are to be expected, and

it is then difficult to deduce evidence as to the internal arrangement of the atoms. Silver and gold particles are found to be crystalline and to show precisely the same space lattice as the macroscopic gold crystals. The size of the particles agrees with that found by other methods. Even in the smallest gold particles, which are much too small to be observed with the ultramicroscope, the characteristic space lattice is observed. Old specimens of silicic acid and stannic acid gels exhibit well-marked crystalline interference figures in addition to the characteristics of amorphous substances, and probably represent substances which are at the point of crystallising. Typical organic colloids (albumin, gelatin, casein, cellulose, starch, etc.) appear to be amorphous; the colloid particles therefore probably consist of individual molecules or of groups of irregularly orientated molecules.

H. W.

Colour of Colloids. III. and IV. WILDER D. BANCROFT (*J. Physical Chem.*, 1919, **23**, 154—185, 253—282. Compare this vol., ii, 102, 187).—Theoretical papers in which the discussion commenced in the previous papers is continued. III deals with the effects produced by reflection from natural objects and its influence on visibility. In IV the influence of interference and diffraction of light is considered.

J. F. S.

Influence of Substitution in the Components of Binary Solutions Equilibria. XVII. Binary Solutions Equilibria of Diphenylamine with Phenols and their Derivatives.

ROBERT KREMAN and RUDOLF SCHADINGER (*Monatsh.*, 1919, **40**, 35—56. Compare A., 1918, ii, 68, 69; this vol., ii, 15, 55, 143).—Melting-point curves have been constructed for the binary systems formed between diphenylamine on the one hand and α -naphthol, β -naphthol, pyrogallol, or one of the three dihydroxybenzenes on the other. In no case is a compound formed between the components, but only simple eutectics. This is attributed to steric influences and to a diminution of the heteropolarity. The three binary systems formed between diphenylamine and the three nitrophenols also yield only simple eutectics and no compounds. Picric acid and diphenylamine form an equimolecular compound.

J. F. S.

Influence of Substitution in the Components of Binary Solutions Equilibria. XVIII. Binary Solutions Equilibria between Nitrosodimethylaniline and some Amines.

ROBERT KREMAN and OTTO WIK (*Monatsh.*, 1919, **40**, 57—79. Compare preceding abstract).—Melting-point curves have been constructed for the binary mixtures formed between nitrosodimethylaniline and α -naphthylamine, the three phenylenediamines, acetamide, benzamide, pyridine, quinoline, and acridine. It is shown that a compound, m. p. 84° , is formed between two molecules of nitrosodimethylaniline and one molecule of α -naphthylamine; *m*-phenylene-

diamine and *p*-phenylenediamine each form compounds with two molecules of nitrosodimethylaniline, whilst *o*-phenylenediamine forms an equimolecular compound, m. p. 99°. Two molecules of nitrosodimethylaniline form compounds with one molecule of acetamide and benzamide respectively. One molecule of nitrosodimethylaniline combines with four molecules of pyridine, m. p. 4·3°, whilst in the case of acridine, three compounds were formed consisting of nitroso-compound and acridine in the molecular ratios 2:1, 3:2, and 1:1. In the case of quinoline, no compounds are indicated.

J. F. S.

Investigations on Carbonate- and Chloride-Fusions. PAUL NIGGLI (*Zeitsch. anorg. Chem.*, 1919, **106**, 126—142).—The equilibrium conditions in the system $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{CaO}-\text{CO}_2$ have been studied between 600° and 1000° in an atmosphere of carbon dioxide at atmospheric pressure. The two binary systems $\text{Na}_2\text{CO}_3-\text{CaCO}_3$ and $\text{K}_2\text{CO}_3-\text{CaCO}_3$ have previously been dealt with (A., 1916, ii, 211). The other binary system has now been studied. Sodium and potassium carbonates form a continuous series of mixed crystals, the minimum point on the curve lying at 712° with about 46 mol. % of potassium carbonate. Mixtures of sodium and potassium carbonates containing 50 mol. % of calcium carbonate behave as binary mixtures of the two double salts $\text{Na}_2\text{Ca}(\text{CO}_3)_2$ and $\text{K}_2\text{Ca}(\text{CO}_3)_2$ below 850°, but above this temperature the salts readily lose carbon dioxide. The double salts form a continuous series of mixed crystals. Mixtures of the three carbonates containing less than 50 mol. % of calcium carbonate behave up to 900° under one atmosphere of carbon dioxide as a ternary system. The equilibrium diagram is given in the form of a triangle with the three simple carbonates as the corner constituents.

In the course of the investigation of the system $\text{Na}_2\text{Cl}_2-\text{Na}_2\text{CO}_3-\text{CaCO}_3-\text{CaCl}_2$, two binary systems have been examined. The examination of the system $\text{CaCl}_2-\text{CaCO}_3$ offers great experimental difficulties. With a large proportion of calcium carbonate, the melts become very viscous at about 700°, and the cooling effects are uncertain. Sometimes, just previous to crystallisation, an emulsion appears to be formed. Formation of oxychloride is almost unavoidable. With 30 mol. % of calcium carbonate, there is a eutectic at about 622°. The system $\text{Na}_2\text{Cl}_2-\text{Na}_2\text{CO}_3$ has a eutectic point at 640°. The examination of the ternary system $\text{Na}_2\text{Cl}_2-\text{Na}_2\text{CO}_3-\text{CaCO}_3$ also offered difficulties on account of the viscous nature of the melts and of the small thermal effects. Two characteristic arrest points were found, at 690° and 640°. The results are shown on a triangular diagram with Na_2Cl_2 , Na_2CO_3 , and CaCO_3 as the corner constituents. The petrological significance of the results of the investigations is discussed.

E. H. R.

The Propagation of Flame in Mixtures of Acetylene and Air. WALTER MASON and RICHARD VERNON WHEELER (T., 1919, **115**, 578—587).

Calculation of Temperatures of Explosion. A. V. BLOM (*Z. ges. Schiess. u. Sprengstoffw.*, 1916, **11**, 219—221; from *Chem. Zentr.*, 1919, i, 268).—The maximum temperature obtained during explosion may be calculated from the formula: (1) $dQ = C' \cdot dt$, where Q is the heat of combustion and is determined calorimetrically or calculated from thermochemical data, and C' the true molecular specific heat at constant volume. From the values for the specific heat of polyatomic gases obtained during recent years (the calculations of temperature, particularly for triatomic gases and the older linear formulæ, are useless), the following functions (2) for C' are obtained: H_2 , $C' = 4.70 + 0.90 \times 10^{-3}t$; O_2 , N_2 , CO , $C' = 4.90 + 0.90 \times 10^{-3}t$; CO_2 , $C' = 7.98 + 2.44 \times 10^{-3}t$; H_2O , $C' = 3.84 + 4.68 \times 10^{-3}t$. $C' = \alpha + \beta t + \gamma t^2 + \delta t^3 + \dots$ (The temperature-coefficients express the mobility of the atoms in the molecule.) Using the general expression $C' = \phi(t) = \alpha + \beta t$, and substituting in equation (1), the formula $dQ = (\alpha + \beta t)dt$ is obtained, which, on integration, becomes $Q = \alpha t + (\beta/2)t^2$ (3). If the relative quantities of gases formed by explosion are $[H]$, $[N]$, $[O]$, $[CO]$, $[CO_2]$, and $[H_2O]$, the following coefficients are derived from formula (2):

$$\alpha = 4.70[H] + 4.90\{[N] + [O] + [CO]\} + 7.98[CO_2] + 3.84[H_2O],$$

$$\beta = 0.9\{[H] + [O] + [N] + [CO]\} + 2.44[CO_2] + 4.68[H_2O] \cdot 10^{-3}.$$

The temperature of explosion may then be calculated by substituting these coefficients in equation (3). H. W.

The Determination of the Temperatures Reached in Explosive Reactions. HENRI MURAOUR (*Compt. rend.*, 1919, **168**, 995—997).—The two indirect methods commonly used for evaluating the temperatures reached in explosive reactions require the assumption of the composition of the gas at the moment of the explosion, and according as it is assumed that methane exists at the moment of the explosion or that it is formed during the cooling, so wide differences in temperature may be obtained.

Working with powders, which gave gases rich in methane, and using an "erosion" bomb with sudden liberation of the gases, the author finds that the greater part, if not the whole, of the methane contained in the products of combustion of powders is formed during the period of cooling. Thus, then, in calculating the temperatures of explosion, the most accurate results will be obtained by reverting the whole of the methane to $CO + H_2$. As a result of this, it is shown that the temperature of explosion of powders does not increase when the density of the charge is increased.

W. G.

The Thermal Decomposition of Phosphine. MAX TRAUTZ and DIVACAR S. BHANDARKAR (*Zeitsch. anorg. Chem.*, 1919, **106**, 95—125).—The rate of decomposition of phosphine into phosphorus and hydrogen has been measured manometrically in a porcelain vessel at temperatures between 845° and 956° . Above the latter temperature, the decomposition is too rapid for measurement. The

reaction is of the first order, and is the first example of a gas reaction of this order to be recorded. Only above 945° , however, is the reaction uninfluenced by the walls of the vessel, and therefore a pure gas reaction. Above this temperature, the temperature-coefficient is about 1.8, but below 945° it sinks rapidly, owing to the growing predominance of the surface reaction. By means of the theory of gas reactions, the "heat of activation" and the size of the phosphine molecule are calculated. From the value of the former quantity, it is calculated that the limit of photosensitivity for phosphine, apart from the infra-red, lies at about 329μ . This research provides the first experimental proof of the theory of gas reactions (A., 1918, ii, 151), and also confirms the opinion that a gas reaction can be freed entirely from the influence of the surface of the reaction vessel if the temperature be raised sufficiently high.

The reaction appears to be retarded by water vapour and accelerated by copper, but the differences observed scarcely fall outside the limits of error of the experiments. E. H. R.

Catalysis. XI. The Le Chatelier-Braun Principle from the Point of View of the Radiation Hypothesis. WILLIAM CUDMORE McCULLAGH LEWIS (T., 1919, 115, 710—712).

The Atomic Ether, Hydrogen Atom, and Planck's Energy Quantum. L. ZEHNDER (*Ber. Deut. physikal. Ges.*, 1919, 21, 118—125).—A theoretical paper in which the author puts forward a theory of an atomic ether. This substance is supposed to be made up of spherical ether atoms which are very small in comparison with atoms of matter; they are completely elastic, and move with a velocity comparable with that of light. A sheath of ether atoms surrounds every material atom and molecule, and all matter is pervious to ether atoms, so that there is no such state as an ether vacuum. The author is of opinion that differences in velocity of ether atoms constitute many of the physical phenomena; for example, electricity is nothing but the heat of the ether, and light, percussion of the ether. The electron is made up of a definite number of ether atoms with an increased heat content. The increase of mass of an electron with increase in velocity is attributed to the carrying of more ether atoms by the electron. This theory is examined in connexion with several physical laws, and found not to be at variance with them. The hydrogen atom is supposed to be spherical, made up of a perfectly elastic nucleus surrounded by an imperfectly elastic ether sheath. J. F. S.

Mechanical Philosophy and Surface Tension. FRED G. EDWARDS (*Chem. News*, 1919, 118, 270—271).—A theoretical paper in which it is shown that the difference in thermal energy of an electron inside a liquid and a free electron may be measured by the relative energies of the positive ether atom. The energy of the positive atom of free ether is 1.058 erg, and may be calculated

by the equations $U = \frac{3}{2}pv = \frac{3}{2}(5175 \times 10^{17})(1.39 \times 10^{-24})$ C.G.S., $U = \frac{1}{2}mC^2 = 0.4C^2 \times 10^{-24}$ C.G.S. From these formulæ, the velocity (C) of the ether atom is found to be 5.193×10^{10} , or $3\sqrt{3} \times 10^{10}$ cm./sec. This value is $\sqrt{3}$ times the radiation velocity, that is, $\tan 60^\circ$ times the radiation velocity, thus proving that the path of the ether atom coincides with the four edges of a regular tetrahedron. This completes the theory of an atomic ether, previously published (*ibid.*, 1919, **118**, 183), and shows that the atom does not reciprocate in a rectilinear path, which would be the hypothetical alternative motion in a dodecahedral formation with double plena. In dilute solution, the intrinsic molecular pressure of water is found to be 4.51119×10^{11} dynes, which is about forty-one times larger than the generally accepted estimate. This intrinsic pressure can be exactly determined from the heat of neutralisation, so that the unknown term dp/dT of the Clausius equation ($dp/dT = L/(T[v_2 - v_1])$) can be calculated. Further, if the Eötvös formula is accepted, the surface tension of a single molecule is obtainable with the weight of the molecule or molecular aggregate, and as the periodic specific volumes and periodic specific entropies of the elements are measurable, they can all be shown to be functions of the atomic shapes, which recur in accordance with the periodic system when the chemical atoms are assumed to be built up symmetrically with the ether atom as the tetrahedral unit.

J. F. S.

Theory of Allotropy: Allotropes and Allotropoids.

MAURICE COPISAROW (*Chem. News*, 1919, **118**, 265—266).—Allotropy is defined as the capacity of an element to exist in forms differing in the mode of their intramolecular linking; it is to be regarded as a function of the valency. From this definition, it becomes possible to deduce the number of allotropes of a given element. Univalent elements can exist in only one allotropic modification, bivalent elements in two forms: (*a*) as a molecular structure in which both valencies of the elements are fixed, (*b*) as a molecular structure in which some valencies are free. In the case of trivalent elements, two allotropes are possible: (*a*) a saturated molecular structure in which all valencies are fixed, (*b*) an unsaturated molecular structure in which some valencies are free. Quadri-, quinq-, and other multi-valent elements may exist in three allotropic modifications: (*a*) a rigid molecular form in which all valencies are fixed, (*b*) a rigid molecular form in which some valencies are free, and (*c*) a non-rigid molecular form in which some valencies are free. It thus follows that valency and the saturation or fixation of the atoms, and not the number of atoms, play the predominant part in the determination of allotropes, and consequently allotropy becomes the capacity of an element to exist in forms differing in the mode of their intramolecular structure. Molecular forms differing in the number of atoms or the distribution of linkings, but all belonging to the same type of linking, can be termed allotropoids. These molecular forms serve as the transi-

tion stage between polymorphism and allotropy, and can be compared with cryptoisomeric substances. J. F. S.

The Hollandus Writings : a Forgery in the Second Half of the Sixteenth Century. PAUL DIERGART (*Chem. Zeit.*, 1919, 43, 201).—A reasoned statement showing that the works attributed to Isaak and Johann Isaak, of Holland, are forgeries of a date somewhere in the second half of the sixteenth century. J. F. S.

The Death of Scheele. LUCIANO P. J. PALET (*Anal. Soc. Quím. Argentina*, 1919, 7, 44—48).—The author directs attention to an error widely disseminated in chemical and toxicological literature that Scheele died from the effects of the inhalation of hydrogen cyanide, which he discovered. The error seems to have arisen from the confusion of the following facts. In 1775 Scheele discovered hydrogen arsenide, and in 1782 hydrogen cyanide. In 1813 the toxicity of the latter gas was demonstrated by Gehlen, also a Swede, who died in 1815 from the effects of poisoning with hydrogen arsenide. Scheele died in 1786 of phthisis. W. S. M.

Loosening of Fixed Glass Parts (Stopcocks, etc.) by means of Hydrogen Peroxide. SCHWARZE (*Münch. Med. Woch.*, 1918, 65, 1327; from *Chem. Zentr.*, 1919, ii, 83).—Glass stoppers, stopcocks, etc., which have become fixed may be loosened by immersion in undiluted hydrogen peroxide solution. H. W.

Device for Removing Plugs from Stopcocks. VERNON C. ALLISON (*J. Ind. Eng. Chem.*, 1919, 11, 468).—The apparatus consists of a wooden vice, one jaw of which is hollowed so that it fits over the handle and presses against the wide end of the barrel of the tap, whilst the other jaw carries a pin, by means of which a steady pressure can be exerted against the narrow end of the tap. Almost any tap which has "stuck" can be loosened by using this vice. W. P. S.

Inorganic Chemistry.

The Systems Chlorine, Hypochlorous Acid, Sodium Hypochlorite. DE MALLMAN (*Compt. rend.*, 1919, 168, 1114—1117). —To determine the amounts of free chlorine x , chlorine as hypochlorous acid y , and chlorine as sodium hypochlorite z , in an aqueous solution containing chlorine in the three forms, the following process is recommended. The total active chlorine, α , is first determined, giving $x + 2y + 2z = \alpha$, and if this is determined iodometrically, the mixture with potassium iodide being acidified with a known volume of $N/5$ -hydrochloric acid, then the loss in acidity,

β , may be subsequently determined, and expressed in terms of chlorine gives $y + 2z = \beta$. If, now, air is bubbled through a given volume of the original solution for five minutes, the whole of the free chlorine is removed, and may be estimated iodometrically, giving x , and thus the three unknowns may be determined. If sodium chloride is present, the value for x is slightly too high, a portion of the chlorine present as hypochlorous acid being carried over. As a result of numerous experiments, the author concludes that when chlorine, hypochlorous acid, and sodium hypochlorite in aqueous solution are mixed, there is produced, in reality, the reversible reaction $\text{Cl}_2 + \text{NaOCl} + \text{H}_2\text{O} \rightleftharpoons 2\text{HClO} + \text{NaCl}$. W. G.

Existence of Polythionic Chlorides in Solutions of Sulphur in Sulphur Monochloride. G. BRUNI and M. AMADORI (*Atti R. Accad. Lincei*, 1919, [v], **28**, i, 217—228).—The cryoscopic behaviour of sulphur monochloride in bromoform solution corresponds with the formula S_2Cl_2 . A mixture of sulphur monochloride and sulphur depresses the freezing point of bromoform by an amount less than the sum of the depressions produced by the two solutes taken separately. The conclusion is drawn that such a solution contains polythionic chlorides in equilibrium with their components, the divergence of the actual from the calculated depression indicating approximately the formula of the complex chloride. In bromoform solution, the highest such complex compound definitely known to be present is the tetrathionic chloride, S_4Cl_2 , but chlorides richer in sulphur probably exist in solutions of sulphur in the monochloride. To the presence of these polythionic chlorides are due the formation of polythio-derivatives by the action, substitutive in character, of sulphur monochloride on organic substances, and also the fact that, in the cold vulcanisation of caoutchouc by means of sulphur monochloride, products may be formed containing sulphur in excess of the ratio S:Cl. T. H. P.

The System SiO_2 . A. SMITS and K. ENDELL (*Zeitsch. anorg. Chem.*, 1919, **106**, 143—148).—In an earlier paper (A., 1913, ii, 318), an attempt was made to explain the system SiO_2 in terms of the authors' theory of allotropy, two pseudo-components being assumed. To account for a metastable transition point, however, the system must be at least ternary, and consequently the solution put forward in the earlier paper is incorrect. An assumption of three pseudo-components is now made, of which two are assumed to be in a state of invariable equilibrium, and are treated in the equilibrium diagram as one component. The discussion is limited to the α - and β -cristobalite portion of the system, and does not deal with tridymite. E. H. R.

Limits of Formation of Mixed Crystals between Potassium Chloride and Sodium Chloride. R. NACKEN (*Sitzungsber. K. Akad. Wiss. Berlin*, 1918, 192—200; from *Chem. Zentr.*, 1919, i, 77. Compare Kurnakov and Shemtschushni, A., 1906, ii, 443).—The experiments were undertaken with the

object of investigating the separation curve with greater accuracy than has yet been possible with cooling curves, which can show considerable inaccuracies due to the tardiness with which equilibrium is established in the solid phase. The method adopted was that of Day and Sosman (A., 1911, ii, 496), and the region of existence of mixed crystals was found to be considerably smaller than has been previously assumed. The critical separation temperature lies slightly below 500° (according to previous determinations, $373\text{--}405^{\circ}$), the composition of the maximum at about 65 mol. % NaCl. In a mixture of the two components, pure sodium chloride appears to be stable below 300° , pure potassium chloride slightly below 250° .

Investigation of the various mixtures was carried out by the aid of their refractive indices, using suitable mixtures of liquids; the latter were made up from eugenol with either oil of cinnamon or sandal-wood oil or Bergamot oil. H. W.

Rearrangement of Acid Salts of Dibasic Acids in Aqueous Solutions into Normal (Neutral) Salts and Free Acids. II. TH. SABALITSCHKA (*Ber.*, 1919, 52, [B], 567—584. Compare A., 1917, i, 699, 700).—Some further experiments of a more exact nature are described, demonstrating that acid salts of dibasic acids exist in solution to a greater or less extent as a mixture of normal salts and free acids.

I. *Dialysis of Aqueous Solutions.*—The diffusates of solutions of sodium and potassium hydrogen sulphates contain quantities of free sulphuric acid which indicate that about 43% or 28.3% respectively of the acid salts have been transformed in solution into mixtures of free acid and normal salts. Similarly, the diffusate of potassium hydrogen camphorate contains an excess of the normal salt, the free acid being so slightly dissociated that it cannot diffuse so rapidly as its ion.

II. *Crystallisation.*—A 32% solution of potassium hydrogen sulphate, left at $5\text{--}10^{\circ}$ for a few days, deposits neutral crystals. A 50% solution of sodium hydrogen sulphate (salt to water, 1:1), left at $5\text{--}10^{\circ}$, gives crystals consisting of Na_2SO_4 91.754%, NaHSO_4 5.867%, H_2O 2.38%. A solution of potassium hydrogen camphorate, made by dissolving 5 grams of the acid in 250 c.c. of 0.1*N*-potassium hydroxide and evaporating to 180 c.c., deposits pure camphoric acid on cooling.

III. *Precipitation with Alcohol.*—A solution of sodium hydrogen sulphate (20 grams = 17.506 grams of NaHSO_4 , in 50 c.c.), mixed with alcohol until a turbidity just appears (200 c.c.), gives a precipitate, during two days, of pure sodium sulphate, leaving only 4.2% of the acid salt in solution. The alcohol may be recovered easily. (Compare the experiment with the potassium salt, *loc. cit.*)

IV. *Extraction of the Acid [Organic] with Ether.*—Quantitative experiments with the camphorate are described (*loc. cit.*).

J. C. W.

Electrolytic Dissociation of Sodium Iodide. BROR HOLMBERG (*Svensk. Kem. Tidskr.*, 1918, pp. 6; from *Chem. Zentr.*, 1919, i, 211).—The author finds that the law of mass action is strictly applicable to the ionic dissociation of sodium and potassium iodides at concentrations from 1*N* to 0·05*N*. The method of experiment is based on the fact that the velocity of racemisation of *l*-iodosuccinic acid is dependent on the concentration of iodine ions in the solution. H. W.

New Method for the Preparation of Ammonium Iodide. E. RUPP (*Apoth. Zeit.*, 1918, **33**, 406, 473; from *Chem. Zentr.*, 1919, i, 10. Compare Brocksmit, A., 1918, ii, 16).—The following is the most suitable method of preparing ammonium iodide from ammonia and iodine in the presence of hydrogen peroxide. Powdered iodine (10 parts) is shaken with official hydrogen peroxide solution (60 parts) and gradually treated with ammonia solution (30 parts), when the iodine passes into solution. If necessary, hydrogen peroxide is added drop by drop until further evolution of gas does not occur and the solution is pale yellow in colour. The filtered solution is warmed on the water-bath, when it becomes colourless; after evaporation, the salt is rubbed with a small quantity of ammonia and dried. H. W.

Ammonium Silicate. II. Ammonia and Silicoformic Acid [Dioxodisiloxane]. ROBERT SCHWARZ (*Ber.*, 1919, **52**, [B], 601—606. Compare A., 1917, ii, 31).—In the experiments on the solubility of silicic acid in ammonia solutions described previously, it was doubtful whether neutralisation or merely the production of a colloidal solution had occurred. It is now shown that dioxodisiloxane, made by leading trichloromonosilane vapour into water, reacts with ammonia solution just as it does with potassium or sodium hydroxide, that is, according to the equation $\text{Si}_2\text{H}_2\text{O}_3 + 4\text{NH}_4\cdot\text{OH} = 2(\text{NH}_4)_2\text{SiO}_3 + 2\text{H}_2 + \text{H}_2\text{O}$. The reaction is completed in about twenty minutes, and most of the silica, with which specimens of dioxodisiloxane are usually contaminated, remains as a precipitate. J. C. W.

Influence of Different Ammonium Salts on the Precipitation of Magnesium Hydroxide. E. BRUNNER (*Helv. Chim. Acta*, 1919, **2**, 277—279).—If the usual explanation of the influence of ammonium chloride in preventing the precipitation of magnesium hydroxide is correct, namely, that the effect is due to the mass action of the ammonium ions provided by the salt, then a less completely dissociated salt, like ammonium sulphate, would have a weaker influence. Experiments are described which prove that the reverse is the case. Under equivalent conditions, ammonia solution produces less precipitate from magnesium sulphate when ammonium sulphate is present than when the preventative is ammonium chloride, and a mixture of the two chlorides gives much more precipitate than a mixture of the two sulphates. Even in

the absence of an ammonium salt, the sulphate gives less precipitate than the chloride.

The explanation is to be found in the greater dissociation of magnesium chloride. The sulphate dissociates largely as follows: $2\text{MgSO}_4 \rightleftharpoons \text{Mg}^{++} + [\text{Mg}(\text{SO}_4)_2]''$ (compare Bredig, A., 1894, ii, 226), and therefore gives fewer magnesium ions than the chloride. The addition of ammonium sulphate depresses the normal dissociation still further, which explains the great stability of cerbolite, $\text{MgSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ (Jones and Caldwell, A., 1901, ii, 375).

J. C. W.

The Nature of Subsidiary Valencies. XXIII. Thermal Degradation of the Ammines of Zinc. FRITZ EPHRAIM (*Ber.*, 1919, 52, [B], 957—964. Compare this vol., 286, 287, 291).—The expected analogy between the ammines of copper and zinc has led to a study of the latter in which only a slight parallelism is observed between the two series. The following ammines have been investigated, their temperature of decomposition being placed within brackets after each number: zinchexamine chloride (57·5°), tetra-ammine (92°), diammine (not below 200°); zinchexamine bromide (62°), tetra-ammine (143°), diammine (?); zinchexamine iodide (65°), tetra-ammine (199°), diammine (?); zinchexamine nitrate (31·5°), tetra-ammine (206°), triammine (?); zinchexamine formate (−4°), tetra-ammine (51·5°), $\text{Zn}(\text{HCO}_2)_2 \cdot 2\cdot5\text{NH}_3$ (63°), diammine (not below 100°); zincpentamine oxalate (18°), diammine (?); zinchexamine thiocyanate (0°), tetra-ammine (86°), the triammine possibly exists; zincoctamine benzoate (−3°), pentamine (21°), triammine (56°), diammine (not below 100°); zincpentamine sulphate (19°), tetra-ammine (98·5°), triammine (185°), diammine (?).

H. W.

Cryoscopic Study of Couples. Cadmium Bromide—Alkali Bromide. E. CORNEC and G. URBAIN (*Bull. Soc. chim.*, 1919, [iv], 25, 215—218).—A study of the freezing-point curves of aqueous solutions of cadmium bromide with the different alkali bromides and hydrogen bromide reveals the existence in solution of double salts of the type $\text{CdBr}_2 \cdot 2\text{MBr}$, where M may be hydrogen, potassium, sodium, or ammonium.

W. G.

Cryoscopic Study of Couples. Cadmium Chloride—Alkali Chloride. E. CORNEC and G. URBAIN (*Bull. Soc. chim.*, 1919, [iv], 25, 218—222. Compare preceding abstract).—In the case of cadmium chloride and alkali chlorides, a cryoscopic study reveals the existence in aqueous solutions of double salts of the type $\text{CdCl}_2 \cdot \text{MCl}$, where M may be hydrogen, potassium, sodium, or ammonium.

W. G.

Lead Nitrate-Hypophosphate and Related Substances. EDMUND VON HERZ (*Z. ges. Schiess. u. Sprengstoffw.*, 1916, 11, 365—367, 388—389; from *Chem. Zentr.*, 1919, i, 271).—Attempts

to use phosphorus and its compounds in the manufacture of explosives have generally resulted in failure, but a highly explosive double compound, $\text{Pb}(\text{NO}_3)_2 \cdot \text{Pb}(\text{H}_2\text{PO}_2)_2$, may be prepared when lead nitrate, as source of oxygen, is mixed in the moist state with lead hypophosphite. Its rate of detonation is greater than that of mercury fulminate and approximately equal to that of lead azide. Its small energy content, or the relatively small volume of gas liberated by its decomposition (117 litres per kilo., as contrasted with 230 litres with lead azide and 314 litres with mercury fulminate), inhibits its use as initial explosive in the usual amount of charge. Its suitable sensitiveness and detonation point, its great stability, and the high temperature of its flame render it very appropriate for percussion-fuse compositions. It is prepared by adding a hot saturated solution of lead nitrate (331 grams) to a boiling saturated solution of calcium hypophosphite (170 grams), and cooling the mixture rapidly with efficient stirring, when white, crystalline lead hypophosphite separates. Two hundred and fifty grams of the latter are added with stirring to a boiling solution of lead nitrate (500 grams) in water (1.5 litres), and rapidly cooled. The double compound, dried at $40\text{--}50^\circ$, is only practically useful when it is obtained as a heavy, granular, crystalline powder; it is less suitable in the form of needles or as a felted, voluminous mass.

H. W.

New Atomic Weight Determinations. [Thorium-lead and Scandium.] O. HÖNIGSCHMID (*Zeitsch. Elektrochem.*, 1919, **25**, 91—97).—An account is given of a series of atomic weight determinations of thorium-lead and scandium. Lead from thorite was converted into chloride, and the ratios $\text{PbCl}_2 : 2\text{Ag}$ and $\text{PbCl}_2 : 2\text{AgCl}$ determined. From these experiments, the values 207.88 (one expt.) and 207.91 (two expts.) were obtained respectively. The mean value for Pb_{Th} is 207.90 ± 0.013 , which is the highest value yet obtained for any variety of lead. Further experiments were also made by the same method with lead from three different samples of thorianite of unknown origin, but probably from Ceylon. The following mean values were obtained: (1) 207.21, (2) 206.91, and (3) 206.84 for the three samples. From the results of the investigation, the author is of the opinion that a lead isotope of atomic weight 208.1 probably exists, and that in all probability $\text{Th-}D$ is not absolutely stable, but has a very long average life. The general question of the origin of the various lead isotopes is discussed, and the recent work of Soddy, Fajans, and others reviewed in this connexion. It is pointed out that the whole of the atomic weight determinations of scandium have been made by the sulphate method, and that very divergent results, fluctuating between 44.1 and 45.2, have been obtained by different investigators. The author has therefore made a series of analyses of the bromide by the Richards method. The bromide was prepared by heating the oxide in a quartz tube with carbon and bromine vapour, and the product purified by sublimation in a quartz tube. The

product was collected and treated generally in the way adopted by the author in his determinations of the atomic weights of uranium and thorium (A., 1916, ii, 484, 510). The sublimation of scandium bromide does not take place below about 1000° , at which temperature the substance has not melted. It is also found that after sublimation the quartz tube has been attacked to a slight extent by the bromide, according to the equation $4\text{ScBr}_3 + 3\text{SiO}_2 = 3\text{SiBr}_4 + 2\text{Sc}_2\text{O}_3$. The amount of the reaction is not great, and was determined by weighing the quartz tube before and after the experiments. A correction based on this action was introduced into the final calculations. For the purpose of reducing the weighings to vacuum standard, the specific gravity of scandium bromide was determined, and the value 3.910—3.913 obtained. Two specimens of scandium were used in the experiments: I, supplied by R. J. Meyer, and II, supplied by Sterba-Böhm. These specimens had been purified by different methods, and a spectroscopic examination by Haschek indicated that they were both absolutely pure—so pure, in fact, that the very persistent ytterbium line $\lambda = 3694.37$ was not present in the spectra. Specimen I gave a mean value for the atomic weight $\text{Sc} = 45.105$ (eight expts.), and specimen II the value $\text{Sc} = 45.093$ (ten expts.), the mean of the whole being 45.099 ± 0.014 , a value which is rounded to 45.10, and is one unit higher than the value 44.1, at present adopted by the International Atomic Weight Committee. J. F. S.

Blue Copper Oxide. H. E. SCHENCK (*J. Physical Chem.*, 1919, 23, 283—285).—A mixture of copper sulphate and aluminium containing approximately 5% of copper oxide was dissolved in water and precipitated with a slight excess of sodium hydroxide, filtered, thoroughly washed, and dried at 110° . The dried precipitate was very light blue in colour, and on grinding to a very fine powder and heating first in a Bunsen flame and then in a blowpipe flame, the colour changed to a light greyish-blue with no signs of blackening. A similar mixture containing twice as much copper oxide remained blue after heating in the Bunsen flame, but showed signs of blackening when heated in the blowpipe. The view is expressed that alumina stabilises the blue oxide of copper, and that the change from blue to black is due to an agglomeration of the particles. Similar preliminary experiments were made with other oxides; these were in all cases made with 5% of the oxide to 95% of alumina; manganous oxide is pink before heating and brown after heating; cobalt oxide is white with a blue tinge, but deep blue after heating, and nickel oxide is green before heating, but yellow after heating. J. F. S.

The Nature of Subsidiary Valencies. XX. Ammines of Cuprous and Lithium Salts. FRITZ EPHRAIM (*Ber.*, 1919, 52, [B], 236—241. Compare A., 1918, ii, 313).—The author hoped to find simple rules governing the formation of ammines by the salts of univalent metals, but has met with quite conflicting conditions

in the case of silver (*ibid.*), aurous, cuprous, thallous, and lithium compounds, as may be seen from the following summary of the properties of the haloids. Lithium salts yield tetrammines, which increase in stability from chloride to iodide. The same order of stability, with smaller and smaller differences, is met with among the tri- and di-ammines, but in the case of the monoammines the order is reversed, as it is with the silver haloid triammines. Cuprous haloids form triammines of almost identical stability, whilst aurous salts only give diammines. Thallous salts, owing no doubt to the great atomic volume of thallium, do not combine with ammonia. The lack of co-ordination with the generalisations made in earlier papers is obviously due to the fact that these were made on hexammines, which the salts of univalent metals do not form at all.

The following list records the temperatures at which the vapour pressures of the ammines are 760 mm. Triammines are formed by cuprous chloride, 46.3° ; bromide (pale green), 49.3° ; and iodide (almost white), 50° . Diammines only are given by cuprous thiocyanate and nitrate, whilst the cyanide only forms a monoamine. (The present results differ from Lloyd's, A., 1908, ii, 847.) Tetrammines are produced by lithium chloride, 12° ; bromide, 53.8° (Bonnefoi, A., 1900, ii, 478); iodide, 90.5° ; nitrate, a syrup, more stable than the chloride tetrammine; chlorate, a fairly mobile liquid; and perchlorate, a solid which decomposes and liquefies at the ordinary temperature.

J. C. W.

The Nature of Subsidiary Valencies. XXII. Thermal Degradation of Ammines of Copper. FRITZ EPHRAIM (*Ber.*, 1919, 52, [B], 940—957. Compare Ephraim and Bolle, A., 1916, ii, 104).—The present communication deals mainly with the stability of the intermediate ammines of copper, and forms the first of a series of such investigations, the theoretical discussion of which is withheld pending the accumulation of more comprehensive data.

The experiments were performed by saturating the requisite salt with ammonia at a low temperature in a bulb blown at the bottom of a small Y-tube; the temperature of the ammine was then gradually raised and maintained constant at those points at which gas was noticeably evolved until evolution of gas practically ceased, the composition of the residue being deduced from the loss in weight. In general, three cases present themselves: (1) the ammine is stable up to a definite temperature, slightly above which ammonia is rapidly evolved, and the next lower ammine is formed; (2) a continuous series of solid solutions exists between two well-defined ammines; (3) the ammine yields solid solutions initially, which are suddenly discontinued, and ammonia is rapidly evolved to the next lower stage, or, conversely, a sudden evolution of ammonia is followed by the formation of solid solutions.

Cupric chloride gives the following ammines: $\text{CuCl}_2 \cdot 2\text{NH}_3$, which decomposes below 270° ; $3\text{CuCl}_2 \cdot 10\text{NH}_3$, formed at 105° and stable to 124° , when it yields the diammine; $\text{CuCl}_2 \cdot 5\text{NH}_3$, which below

105° forms solid solutions, which attain the composition $\text{CuCl}_2 \cdot 6\text{NH}_3$ at about -15°. Cupric bromide yields $\text{CuBr}_2 \cdot 2\text{NH}_3$, decomposing at about 260°; $3\text{CuBr}_2 \cdot 10\text{NH}_3$, decomposing at 155°; $\text{CuBr}_2 \cdot 5\text{NH}_3$, unstable above 116° and yielding solid solutions below this temperature, which have the composition $\text{CuBr}_2 \cdot 6\text{NH}_3$ at about 0°. Cupric iodide yields solid solutions of hexammine and pentammine, which have the composition of the latter at 119.5°, when $3\text{CuI} \cdot 10\text{NH}_3$ is formed; the latter passes at 147° into the diammine. Copper sulphate gives a pentammine, which at about 99° is converted into the tetra-ammine, which slowly loses ammonia at 141.5°, forming the diammine. Copper nitrate gives a deep blue tetra-ammine, which is converted below 15° into a similarly coloured hexammine and decomposes above 205°, yielding indefinite products. Copper pentammine thiocyanate is converted into the tetra-ammine at 3°, which is stable to 101°, when gas is evolved and a series of solid solutions is formed up to 127°, at which the diammine is formed; decomposition occurs above this temperature. Copper tetra-ammine acetate is converted at about 80° into the diammine, which decomposes at about 175°. Copper pentammine oxalate is slowly converted into the diammine at about 46°; the latter is stable at 170°, but is completely decomposed at a higher temperature. Copper octammine benzoate is stable below -3°, at which temperature it is transformed into the hexammine; the latter decomposes with rising temperature, yielding solid solutions, which at 78° have the composition of the tetra-ammine; at 180°, formation of the diammine is complete, whilst at higher temperatures the material melts and decomposes.

H. W.

Thallous Oxide. ALFRED KÖLLIKER (*Chem. Zeit.*, 1919, **43**, 231).—In this preliminary communication, the author disputes the statement occurring in the literature of the subject that "the greyish-black coating of oxide produced when the metal is exposed to air does not penetrate far into the metal, the latter reappearing when the oxide is dissolved in water." Thallium was prepared from thallium sulphate either electrolytically or by means of zinc, and it was found that the whole of the metal was oxidised in a little time. The thallous oxide formed goes completely into solution, and any of the thallium salts can be precipitated therefrom by the usual precipitants, a property which can be utilised for the separation and purification of thallium salts.

J. S. G. T.

Cerium Nitride. P. FABARON (*Ann. Chim. anal.*, 1919, [ii], **1**, 156).—When metallic cerium is heated in a closed copper tube, the oxygen of the air in the tube combines with the copper and the nitrogen with the cerium. The cerium nitride, CeN_2 , formed has a greyish-black colour and is decomposed by water, yielding ammonia and cerous oxide.

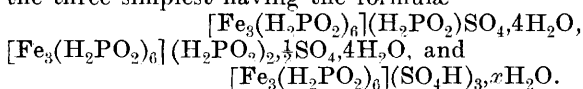
W. P. S.

The Constitution of the Ferric Salts of Hypophosphorous Acid. R. F. WEINLAND and W. HIEBER (*Zeitsch. anorg. Chem.*, 1919, **106**, 15—45).—In addition to the previously known normal

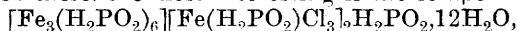
ferric hypophosphite having the composition $\text{Fe}(\text{H}_2\text{PO}_2)_3$, a number of new basic compounds have now been prepared. It has also been found that ferric hypophosphite combines with other inorganic acids to form complex compounds containing both acid radicles, and many such compounds have been characterised and analysed. On account of the stoicheiometric relationships found between the different compounds, and of their singular properties, in particular of their remarkable stability, it has been concluded that the majority of the compounds contain the complex cation $[\text{Fe}_3(\text{H}_2\text{PO}_2)_6]'''$, which is very stable in character and is capable of forming salts both with hypophosphorous acid and with other inorganic acids. In this respect, the ferric salts of hypophosphorous acid are very similar to those of a number of monocarboxylic acids previously described (A., 1916, i, 314).

The normal ferric hypophosphite (3:9) is considered to have the constitution $[\text{Fe}_3(\text{H}_2\text{PO}_2)_6](\text{H}_2\text{PO}_2)_3$. The 3:8 basic salt is prepared in a pure state by mixing solutions of ferric chloride and sodium hypophosphite within certain narrow limits of temperature and concentration. It forms a loose, slightly red powder, and is given the constitution $[\text{Fe}_3(\text{H}_2\text{PO}_2)_6\text{OH}](\text{H}_2\text{PO}_2)_2, 24\text{H}_2\text{O}$. This salt was used for preparing many of the following hetero-acid compounds. Other basic salts isolated contain metal and acid in the ratios 6:15, 3:7, and 3:6 respectively. The last salt is considered to contain a penta-hypophosphite cation, and corresponds with the formula $[\text{Fe}_3(\text{H}_2\text{PO}_2)_5(\text{OH})_3]\text{H}_2\text{PO}_2$.

The hetero-acid compounds were prepared in a number of ways, by the action of acids on the 3:8 basic ferric hypophosphite or by the action of sodium hypophosphite or hypophosphorous acid on ferric salts. Six compounds with sulphuric acid are described, formed by the action of the acid on the 3:8 basic salt under varying conditions. These are all either acid or neutral compounds, the three simplest having the formulæ



For a full description of the others and of the methods of preparation of all the compounds, the original must be consulted. A nitrate is described, and also an explosive perchlorate of the formula $[\text{Fe}_3(\text{H}_2\text{PO}_2)_6](\text{ClO}_4)_2(\text{H}_2\text{PO}_2) + \frac{1}{2}\text{H}_3\text{PO}_2 + 18\text{H}_2\text{O}$. The chlorides and bromides appear to contain complex anions containing iron. Of these, the most interesting is the compound



which is readily obtained crystalline in the form of truncated octahedra of fair size by the action of concentrated hydrochloric acid on the 3:8 basic salt.

The compounds are all sparingly soluble in water, by which many of them are slowly hydrolysed, with formation of the 3:6 basic ferric hypophosphite. They are very stable to acids, and there is little tendency for the ferric iron to be reduced by the hypophos-

phorous acid—a further proof that a complex cation is present. Alkalis, alkali carbonates, and ammonium sulphide decompose them, with formation of ferric hydroxide. Their water of crystallisation is very loosely held, and is often lost on exposure to air.

E. H. R.

Crystalline Substances with Colloidal Properties. Basic Zirconium Sulphates and the Molecular State of Zirconium Sulphate in Aqueous Solution. O. HAUSER and H. HERZFELD (*Zeitsch. anorg. Chem.*, 1919, 106, 1—8).—In aqueous solution, zirconium sulphate is generally supposed to be hydrolysed, with formation of zirconyl sulphates containing the complex anions $\text{ZrO}(\text{SO}_4)_2''$ and $\text{Zr}_2\text{O}_3(\text{SO}_4)_2''$. This view was supported by the existence of a potassium zirconyl sulphate supposed to have the composition $\text{Zr}_2\text{O}_3(\text{SO}_4)_2\text{K}_2$. It is now shown, however, that this formula does not correctly represent the composition of the potassium salt. In reality, the basic compounds formed by the hydrolysis of zirconium sulphate in aqueous solution are much more complex than has been supposed, and three such basic sulphates have now been isolated in crystalline form. Although these compounds are definitely crystalline, yet in solution their properties are essentially colloidal.

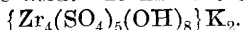
(1) The compound $\{\text{Zr}_4(\text{SO}_4)_3(\text{OH})_{10}\}10\text{H}_2\text{O}$ appears to exist in two forms. One of these has been previously described (A., 1905, ii, 531). The other is prepared by dissolving zirconium sulphate-tetrahydrate in cold water and keeping the 2% solution for several days, when the salt is deposited in the form of needles differing only from the crystals of the first form in their optical properties. The first form is not decomposed by boiling water, whilst the second loses part of its sulphuric acid.

(2) The more basic salt, $\{\text{Zr}_8(\text{SO}_4)_5(\text{OH})_{22}\}8\text{H}_2\text{O}$, is prepared by dissolving anhydrous zirconium sulphate in five times its weight of water and precipitating with alcohol. The precipitate is then dissolved in a little warm water and dialysed, and in the course of a few days the basic salt separates in the form of very characteristic spherical crystals which do not lose their shape when dehydrated.

(3) The salt, $\{\text{Zr}_4(\text{SO}_4)_6(\text{OH})_8\}\text{H}_4\cdot4\text{H}_2\text{O}$, has been previously described (A., 1907, ii, 626), being there given the formula $2\text{ZrO}_2\cdot3\text{SO}_3\cdot5\text{H}_2\text{O}$.

The new formula takes account of its acid properties and explains its ready conversion into either of the salts (1) and (2). It parts with its water very reluctantly, only four molecules being lost at 225° .

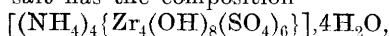
A potassium zirconyl sulphate of definite composition has been prepared by adding, drop by drop, a saturated solution of potassium sulphate to a strong solution of zirconium sulphate tetrahydrate acidified with sulphuric acid. It has the formula



The corresponding zirconyl sulphuric acid could not be isolated.

E. H. R.

Zirconium Alkali Sulphates. ARTHUR ROSENHEIM and JACOB PINSKER (*Zeitsch. anorg. Chem.*, 1919, **106**, 9—14).—Hauser and Herzfeld have shown (preceding abstract) that the crystalline basic zirconium sulphates are semi-colloidal in character, and that their composition is influenced to an unusual degree by the temperature and concentration of the solution in which they are formed. It has now been found that the composition of the double salts formed by zirconium sulphate with sulphates of the alkali metals similarly depends on concentration and other conditions. Two such compounds with ammonium sulphate have been prepared, and are now described. When to a solution of 10 grams of anhydrous zirconium sulphate in 20 c.c. of water is added a solution of 14 grams of ammonium sulphate in 25 c.c. of water and the mixture is allowed to evaporate over sulphuric acid, a double salt separates as a crystalline crust. This salt has the composition



and is evidently the ammonium salt of the zirconyl sulphuric acid described by Hauser (preceding abstract [3]). Subsequently, from the same solution separates a second salt, less basic than the first, and having the composition $(\text{NH}_4)_4\{\text{Zr}(\text{SO}_4)_4\}\cdot 5\text{H}_2\text{O}$. This second salt is apparently only deposited when the acidity of the solution has been sufficiently increased by the separation of the first more basic salt. The second salt dissolves readily in boiling water, and, on cooling, the solution deposits crystals of the first salt.

The double potassium zirconium sulphate, $\text{K}_4\text{Zr}(\text{SO}_4)_4\cdot 3\text{H}_2\text{O}$, prepared by mixing strong solutions of zirconium sulphate and potassium hydrogen sulphate (Rosenheim and Frank, A., 1905, ii, 256), is now found to have a very variable content of water of crystallisation. When normal potassium sulphate is used, a more basic salt is obtained having the composition $\text{K}_4\{\text{Zr}_4(\text{OH})_8(\text{SO}_4)_5\}\cdot 8\text{H}_2\text{O}$. As in the case of the ammonium salts, the product separating from a weakly acid solution is more basic than that from a strongly acid solution. The normal double sulphate, $\text{K}_4\{\text{Zr}(\text{SO}_4)_4\}$ aq., is readily hydrolysed by water at 30°, with formation of complex basic salts, but no product of definite composition could be isolated. On account of their great solubility, basic sodium zirconium sulphates could not be isolated.

All the double salts described have, like the basic zirconium sulphates, colloidal properties. From their heated aqueous solutions, gels are precipitated by electrolytes and by dilute acids. These gels probably consist of colloidal zirconium hydroxide, and only dissolve slowly in excess of strong acid. E. H. R.

The Nature of Subsidiary Valencies. XXI. Gold Compounds. Ammines of Double Salts. Thermal Decomposition of Double Haloids. FRITZ EPHRAIM (*Ber.*, 1919, **52**, [B], 241—254).—The dark brown auric bromide, AuBr_2 , which is obtained by dissolving precipitated gold in bromine, becomes brownish-yellow in an atmosphere of ammonia, and absorbs about 9 molecules of the gas at the ordinary temperature and about

23 molecules in a freezing mixture. Cæsium auribromide resembles auric bromide very closely in its behaviour towards ammonia, and the pale yellow potassium aurichloride also forms at -18° a dark orange-red compound with about 12NH_3 , which effervesces in water with the evolution of free nitrogen.

Auric bromide has the dissociation temperature, in an atmosphere of bromine, 181° , the product being aurous bromide, which is yellow at the temperature of boiling naphthalene, but becomes darker when removed from the bath. It forms a diammine (Meyer, A., 1906, ii, 664). The vapour pressure of auric chloride reaches 760 mm. at 256.5° , but if the salt is left under about 100 mm. pressure at 225° until it acquires a pale yellow colour, that is, until it is changed into aurous chloride, and is then heated further in the atmosphere of chlorine, atmospheric pressure is again reached at 289.5° . That is to say, aurous chloride is only stable in an atmosphere of chlorine over a range of 33° . Aurous chloride diammine has the dissociation temperature 113.5° .

Potassium aurichloride melts at the temperature of boiling mercury, but cæsium aurichloride has a slightly higher m. p. At 440° however, both salts have vapour pressures of about 350 mm.

The fact that aurichlorides and auribromides of the alkali metals behave towards ammonia exactly like the auric salts suggests that they are dissociated by ammonia into the component haloids. The question is therefore raised whether any double salts do, as such, form amines, their tendency in this direction being in great contrast to their affinity for water. J. C. W.

The Attack of Platinum and Gold by the Alkali Hydroxides. L. QUENNESSEN (*Bull. Soc. chim.*, 1919, [iv], 25, 237—240).—A discussion of the results of Nicolardot and Chatelot (compare this vol., ii, 161), and of results published in *Bull. Usines guerre*, 1918, No. 17, 134, from which the author concludes that pure platinum shows the highest resistance to acid reagents, and that, whilst certain alloys of gold and palladium show a high resistance to the action of alkali hydroxides, silver vessels are the more convenient for laboratory purposes. W. G.

A New Method of Preparation of certain complex Compounds of Platinum and of its Analogues. L. TSCHUGAEV (*Bull. Soc. chim.*, 1919, [iv], 25, 234—237).—Potassium platinonitrite reacts with ammonia in the cold to give *cis*-dinitrodiamminoplatinum (compare Tschugaev and Kiltinovic, T., 1916, 109, 1286). The similar iodo-compound, $\text{Pt}_2\text{NH}_3\text{I}_2$, may be obtained by boiling potassium platiniodide in aqueous solution with ammonia. If the ammonia is replaced by methylamine, *di-iododimethylaminoplatinum*, $\text{PtI}_2\text{NH}_2\text{Me}$, is obtained.

The same method may be used for preparing certain complex compounds of rhodium. Thus, if rhodium iodide is warmed in aqueous solution with an excess of ammonia, the compound, RhI_3NH_3 , reddish-brown, microscopic prisms, is obtained.

W. G.

Recovery of Platinum and Alcohol from Potassium Estimations. A. E. SMOLL (*J. Ind. Eng. Chem.*, 1919, 11, 466—467).—The alcoholic filtrates and washings are distilled until all alcohol has been removed; platinum black and water remain in the distillation flask. The distillate is then heated under a reflux apparatus through which a current of warm water is passed so that the temperature of the escaping water is 58°. The top of the reflux apparatus is connected with a condenser, and the heating is continued until all aldehyde has been expelled, as is ascertained by testing drops of the distillate. The alcohol is finally fractionated from a small quantity of sodium hydroxide. [See, further, *J. Soc. Chem. Ind.*, 1919, 444A.] W. P. S.

Solubility of Hydrogen in Palladium Mixed Crystals. G. TAMMANN (*Nachr. Ges. Wiss. Göttingen*, 1918, 72—78; from *Chem. Zentr.*, 1919, i, 338).—A definite limit for the solubility of hydrogen in palladium, analogous to the limits of action of other agents on mixed crystals of gold with silver or copper (A., 1918, ii, 445, 447), is shown to exist at that region of temperature in which a change of position of the two types of atom in the palladium mixed crystal is no longer perceptible. The limit lies at $\frac{1}{4}$ mol. Pd. Taking into account the atomic structure of the palladium mixed crystal, it appears, therefore, that the hydrogen atom can only enter and continue to oscillate at lattice axes which are parallel to the diagonals of the cube which are mainly occupied by palladium atoms. H. W.

Mineralogical Chemistry.

A Chemical Investigation of Banded Bituminous Coal. Studies in the Composition of Coal. FREDERICK VINCENT TIDESWELL and RICHARD VERNON WHEELER (T., 1919, 115, 619—636).

"Blue John" and other Forms of Fluorite. BERTRAM BLOUNT and JAMES HARRY SEQUEIRA (T., 1919, 115, 705—709).

Chubutite, a New Lead Mineral. HÉRCULES CORTI (*Anal. Soc. Quím. Argentina*, 1918, 6, 65—72).—The mineral to which the name *chubutite* is given occurs in the Gobernación del Chubut (Argentina) in radiated masses of obscure, crystalline structure. D 7.95, hardness 2.5, of a yellow colour and easily reduced to powder. Analysis gave:

Al ₂ O ₃ .	Fe ₂ O ₃ .	PbO.	PbCl ₂ .	Sb ₂ O ₃	As ₂ O ₃ .	Insol.	Total.
0.12	0.19	83.30	14.83	0.69	trace	0.76	99.89

This leads to the the formula 7PbO,PbCl₂. The crystalline structure appears to be tetragonal. W. S. M.

A Titaniferous Mineral from the Sierra del Pié de Palo, San Juan (Argentina). LUCIANO R. CATALANO (*Anal. Soc. Quim. Argentina*, 1918, **6**, 35—48 and 83—93).—A detailed account of the chemical analysis of the mineral in question. The formula $\text{FeTiO}_3, \text{MnTiO}_3$ is established. The mineral corresponds in composition with kibelophane, a variety of ilmenite. W. S. M.

Analytical Chemistry.

Colorimetric Determination of the Hydrogen-Ion Concentration in Small Quantities of Solution. A. R. C. HAAS (*J. Biol. Chem.*, 1919, **38**, 49—55).—The preparation of indicator papers which may be used for the rapid estimation of hydrogen-ion concentration is described. The method yields accurate results, and is of considerable value when it is impossible to carry out the electrometric method. J. C. D.

Accuracy of Different Methods of Measuring Small Volumes of Fluid. FREDERICK WILLIAM ANDREWES (*Biochem. J.*, 1919, **13**, 37—44).—A study of the inaccuracies attendant on the methods employed for measurement of small volumes and dilutions, such as are used in serological investigations. J. C. D.

Preparation of Stable Starch and Oxalic Acid Solutions by means of Metallic Mercury. A. JUNK (*Chem. Zeit.*, 1919, **43**, 258).—The solution is treated with a few c.c. of mercury, boiled, and shaken, so that the mercury is finely subdivided; the mercury is allowed to remain in the bottle containing the solution. Such treatment prevents the growth of moulds, etc., in the solutions, and the latter may be kept for years without altering in strength, even when the bottle is opened frequently. W. P. S.

Identification of Iodine in Blood by a Microcrystallographic Method. ULRICH HINTZELMANN (*Zeitsch. physiol. Chem.*, 1919, **104**, 211—216).—The method proposed by Karfunkel (*Dent. med. Woch.*, 1912, 643), which depends on the isolation of crystals of iodohæmatin, is untrustworthy for ordinary use. J. C. D.

Modification in the Technique of Fischer's Reaction for Hydrogen Sulphide. LUCIANO P. J. PALET and AMANCIO FERNANDEZ (*Anal. Soc. Quím. Argentina*, 1918, **6**, 49—51).—On account of the inconvenience in preparing and keeping *p*-aminodimethylaniline sulphate, the following procedure is substituted.

To a drop of dimethylaniline are added 2 c.c. of water, three to four drops of a 1% solution of sodium nitrite, and five drops of 10% hydrochloric acid. The liquid is neutralised with saturated sodium carbonate solution, and the nitroso-base extracted with ether. To the ethereal solution, zinc powder and a few drops of concentrated hydrochloric acid are added. When the reduction is complete, the ether layer is decanted off, 2 c.c. of water and the solution to be tested are added, then concentrated hydrochloric acid, and a few drops of 10% ferric chloride solution. The addition of a little alcohol renders the appearance of the resulting methylene-blue more distinct. It is necessary that hydrochloric acid be present in great excess.

W. S. M.

Estimation of Sulphuric Acid and Sulphates. G. MEILLÈRE (*J. Pharm. Chim.*, 1919, [vii], **19**, 296—297).—In the estimation of sulphates by precipitation as barium sulphate, the precipitate should be collected while the solution is still hot and washed with hot dilute acetic acid solution. In the case of sulphuric acid, this may be neutralised with barium hydroxide solution, using phenolphthalein as indicator, and a very slight excess of the barium hydroxide then added; the mixture is acidified with acetic acid, kept at 100° for two hours, and the precipitated barium sulphate then collected. [See, further, *J. Soc. Chem. Ind.*, 1919, July.]

W. P. S.

Method for the Volumetric Estimation of Sulphates. A. C. D. RIVETT (*Chem. News*, 1919, **118**, 253—254).—The method is intended primarily for works purposes, and depends on double decomposition between moist, precipitated barium oxalate and certain dissolved sulphates, whereby soluble oxalates are produced which may be titrated with potassium permanganate. [For details, see *J. Soc. Chem. Ind.*, 1919, 481A.]

W. E. F. P.

Continuous Process for the Estimation of Nitrogen by Dumas's Method. LUDWIG DEXHEIMER (*Zeitsch. anal. Chem.*, 1919, **58**, 13—19).—To avoid the necessity of cooling the combustion tube after the completion of one estimation and before another can be started, a procedure is described for removing and inserting successive boats while the tube is still hot. The essential feature consists of means for passing the current of carbon dioxide in a reverse direction through the tube while the latter is opened at one end. Provision is also made for oxidising the reduced copper when necessary.

W. P. S.

The Estimation of Total Nitrogen in Soils containing Rather Large Amounts of Nitrates. R. S. SNYDER (*Soil Sci.*, 1918, **6**, 487—490).—If the organic matter of the soil is within the usual average (0.8—3.0%), the Hibbard or the "mercury" methods of carrying out the Kjeldahl digestion give quite accurate

results for total nitrogen, even if 10% of the nitrogen is present as nitrate. Methods for total nitrogen, modified to include nitrate nitrogen, such as Ulsch's method, must, however, be used if the organic carbon content of the soil is lower than 0.5%. W. G.

Estimation of Nitrite and Nitrate Nitrogen in the Presence of other Nitrogen Compounds. TH. PFEIFFER and W. SIMMERMACHER (*Landw. Versuchsstat.*, 1919, **93**, 65—76).—For the estimation of the various forms of nitrogen in such substances as soil extracts, the total nitrogen other than nitric nitrogen is estimated by Kjeldahl's method, using 5 grams of ferrous sulphate. Ammonia nitrogen is estimated by distillation with magnesium oxide; after the ammonia has been removed, the residual solution is treated with 12 grams of magnesium chloride and 3 grams of finely divided copper-magnesium alloy (compare A., 1917, ii, 504), and again distilled to obtain the ammonia derived from the nitrites and nitrates. To estimate the nitrate nitrogen, 75 c.c. of the extract are boiled for one hour with the addition of 1.5 grams of dextrose, 0.3 gram of ferrous sulphate, and 5 grams of sodium carbonate: ammonia and nitrite nitrogen are thus expelled, and the solution is then distilled with copper-magnesium alloy as described. [See, further, *J. Soc. Chem. Ind.*, 1919, July.] W. P. S.

Scrubber for Ammonia Distillations. B. S. DAVISSON (*J. Ind. Eng. Chem.*, 1919, **11**, 465—466).—The scrubber or still-head described consists of a bulb of about 200 c.c. capacity provided with an exit tube at the top, through which the steam, etc., passes to the condenser, and a lower tube or stem for connecting the bulb to the distillation flask. This lower tube extends into the bulb, and is then bent downwards to nearly the wall of the bulb; the tube ends in a small bulb having three openings in the same horizontal plane. The first portion of steam which enters the bulb condenses, and the water flows down about the small bulb, there acting as a scrubbing solution for the remainder of the vapours. W. P. S.

Albuminoid Ammonia Test. EVELYN ASHLEY COOPER and JOSEPH ALAN HEWARD (*Biochem. J.*, 1919, **13**, 25—27).—Potassium permanganate may contain a stable nitrogenous impurity which cannot, as a rule, be removed by prolonged boiling with alkali. This impurity yields ammonia, particularly when the permanganate-alkali mixture is boiled in the dilute condition, and the error involved may be so great as to vitiate the value of the albuminoid ammonia test altogether. [See, further, *J. Soc. Chem. Ind.*, 1919, 438A.] J. C. D.

Identification of Arsenious Acid. Reply to Tunmann. R. WASICKY and A. MAYRHOFER (*Pharm. Post.*, 1918, **51**, 409—410; from *Chem. Zentr.*, 1919, ii, 224).—The authors do not agree with Tunmann's observations (A., 1918, ii, 453) on the

extension of microchemical methods to the detection of arsenic in pharmaceutical preparations, and, further, point out that the destruction of organic matter by concentrated sulphuric acid on the object-glass does not suffice for the detection of arsenic in all possible forms of combination. H. W.

Estimation of Boric Acid. PAUL JANNASCH and FRIEDRICH NOLL (*J. pr. Chem.*, 1919, [ii], **99**, 1—33).—Alcoholic sodium ethoxide solution is recommended for the titration of boric acid solutions in the presence of glycerol; the interfering action of carbon dioxide is thus eliminated. For the estimation of boric acid in minerals, the sample is fused with sodium phosphate and metaphosphoric acid, the boric acid distilled in the presence of methyl alcohol and phosphoric acid, and titrated after the methyl alcohol has been expelled from the filtrate. [See, further, *J. Soc. Chem. Ind.*, 1919, 411A.] W. P. S.

Estimation of Free Carbon Dioxide in Water. HARTWIG KLUT (*Ber. deut. pharm. Ges.*, 1919, **29**, 344—359).—Directions are given for the estimation of free carbon dioxide in water at the source of the latter. The titration is made with sodium carbonate solution, phenolphthalein is used as the indicator, and potassium sodium tartrate is added to the water to prevent interference by ferrous salts. W. P. S.

Estimation of Free Carbon Dioxide in Water. RUDOLF CZENSNY (*Zeitsch. anal. Chem.*, 1919, **58**, 1—12).—To ensure that the correct quantity of indicator is present, a combined solution containing 2·6525 grams of sodium carbonate and 2·5 grams of phenolphthalein is used for the titration of the free carbon dioxide. One hundred c.c. of the water are titrated with this solution; the number of c.c. used, less 0·52 c.c., is multiplied by 1·22 to obtain the mg. of free carbon dioxide per 100 c.c. of water. W. P. S.

Micro-elementary Analysis. ERNST MÜLLER and HERTHA WILLENBERG (*J. pr. Chem.*, 1919, [ii], **99**, 34—44).—A suitable apparatus is described for the determination of carbon and hydrogen in small quantities (2 to 5 mg.) of substance. The apparatus is constructed entirely of glass, rubber connexions are not used, a single burner is used for heating the combustion tube, and the oxygen is prepared from potassium dichromate and Caro's acid. W. P. S.

Efficiency of Potash Absorption Apparatus and Comparative Trials with a New Form of Helical Apparatus. J. FRIEDRICH (*Zeitsch. angew. Chem.*, 1919, **32**, 129—132).—A new form of potash absorption apparatus for combustion analysis is described consisting of two cylindrical vessels of light glass fused one inside the other. The gas enters at the top of the inner vessel

and passes through a hole at the bottom into the annular space between the two vessels. A spiral is moulded on the outer wall of the inner vessel so that its apex leaves only a small clearance in the annular space, and the bubbles of gas emerging from the inner vessel are compelled to follow the spiral path in their passage up to the exit, whilst at the same time the displaced liquid is free to circulate through the narrow clearance between the helix and the outer vessel. At the top an exit orifice is provided, on which is fitted, with a ground-in joint, a bent calcium chloride tube. The whole apparatus, when filled, weighs only about 38 grams and contains 10 c.c. of potash solution. It is compact and not liable to breakage, the whole surface can easily be wiped clean, and if the liquid is sucked back there is ample room in the capacious inner vessel to prevent loss. The path travelled by the bubbles of gas is about 25 cm. long, and yet the resistance pressure of the liquid is equivalent to only 5 cm. The efficiency of this apparatus has been tested comparatively with a number of well-known types of other absorption apparatus with different speeds and quantities of carbon dioxide in air, and the results were most favourable.

J. F. B.

Studies of Acidosis. XIII. A Method for Titrating the Bicarbonate Content of the Plasma. DONALD D. VAN SLYKE, EDGAR STILLMAN, and GLENN E. CULLEN (*J. Biol. Chem.*, 1919, **38**, 167—178).—Blood is drawn with precautions against loss or accumulation of carbon dioxide. Two c.c. of the plasma are measured into a round-bottomed flask of 150 to 200 c.c. capacity, and 5 c.c. of 0.02*N*-hydrochloric acid are added. Carbon dioxide is removed by vigorous shaking, and titration is carried out with 0.02*N*-carbonate-free sodium hydroxide, using neutral-red or phenolsulphonaphthalein as indicator until the colour of the solution matches one of known hydrogen-ion concentration. The results agree well with those given by the carbon dioxide capacity method over a range of bicarbonate concentrations (0.03—0.01*M*) ordinarily encountered in man, even in severe acidosis.

J. C. D.

Microchemical Distinction of Sericite and Talc. O. HACKL (*Verh. geol. Reichsanst. Wien*, 1918, 1; from *Chem. Zentr.*, 1919, ii, 225—226).—The macrochemical distinction of sericite from talc is tedious, since the former frequently contains magnesium and the latter aluminium. The following microchemical method is proposed. A small quantity of the finely powdered specimen is boiled with concentrated hydrochloric acid in a small platinum spoon, the precipitate is allowed to subside, and the supernatant liquid is drawn off with a small pipette and evaporated in a platinum lid to remove the bulk of the acid, which cannot be neutralised, since the process involves the introduction of too large quantities of salt into the solution, whereby further concentration is hindered. The residue is warmed with a small quantity of water containing a trace

of hydrochloric acid; the undissolved matter is allowed to separate, and the clear liquid withdrawn with a capillary pipette. A drop of this solution is tested for potassium with freshly prepared platinic chloride solution, preferably using a cover-glass of quartz; a second drop is tested for aluminium by addition of caesium chloride in the presence of sodium sulphate, which renders possible the formation of the alum. Magnesium is detected by the usual method in a third drop after precipitation of any considerable amount of aluminium by addition of ammonia; the precipitate need not be removed.

H. W.

Estimation of Mercury in Mercury Salicylate. A. COSTANTINO (*Giorn. Farm. Chim.*, 1918, **67**, 7—12; from *Chem. Zentr.*, 1919, ii, 4—5).—Mercury salicylate (0.25 gram) is warmed in a porcelain dish on the water-bath for about six minutes with concentrated sulphuric acid (2 c.c.). The solution is diluted with water to 160 c.c. and electrolysed in a platinum dish during fourteen minutes, a rotating platinum anode and a current of 6 amperes at 5 volts being used; without interrupting the current, the deposit is washed successively with water, alcohol, and ether, and dried in a desiccator. A mercury cathode may be used in place of a platinum dish, in which case the volume of the solution should not be more than 30 c.c., and the current 3 amperes at 7—10 volts. The process is more advantageous than those previously described and more convenient than those of the United States Pharmacopœia, 1916.

H. W.

The Conductivity as Indicator in Titrations with Potassium Permanganate. VICENTE VILLUMBRALES (*Anal. Fis. Quim.*, 1919, **17**, 100—114).—In the titration of ferrous salts by means of permanganate solution, free acid is consumed according to the equation $2\text{KMnO}_4 + 10\text{FeSO}_4 + 8\text{H}_2\text{SO}_4 = 5\text{Fe}_2(\text{SO}_4)_3 + \text{K}_2\text{SO}_4 + \text{MnSO}_4 + 8\text{H}_2\text{O}$. Ordinarily, acid is added in great excess to dissolve the colloidal manganese oxide formed, and the conductivity of the mixture during the titration remains practically constant. In presence of insufficient acid, the conductivity falls with the addition of the permanganate solution until the oxidation is complete, and thereafter remains constant, the end-point being indicated by a sharp angle in the curve. In the oxidation of manganous salts in neutral solution by means of permanganate, acid is formed: $3\text{MnSO}_4 + 2\text{KMnO}_4 + 2\text{H}_2\text{O} = 5\text{MnO}_2 + \text{K}_2\text{SO}_4 + 2\text{H}_2\text{SO}_4$. In this case, the conductivity increases during the titration, and becomes constant on completion of the oxidation.

W. S. M.

Use of Colloidal Silica in Iron Titrations. E. DITTLER (*Chem. Zeit.*, 1919, **43**, 262).—The author confirms the statement by Schwarz and Rolfes (this vol., ii, 170) that colloidal silica, in the presence of manganous salts, prevents the oxidation of hydrogen chloride. [See, further, *J. Soc. Chem. Ind.*, 1919, July.]

W. P. S.

Iodometric Estimation of Chromic Acid. I. M. KOLTHOFF and E. H. VOGELZANG (*Pharm. Weekblad*, 1919, **56**, 514—524).

In the presence of sufficient acid (at least 20 c.c. 4*N*-hydrochloric acid in 100 c.c. of solution), the mixture may be titrated immediately after the addition of the reagents, even in the case of dilute chromate solutions. If insufficient acid is present, too much thio-sulphate is consumed, owing to the occurrence of a side-reaction, the nature of which is not clearly ascertained, although it is shown that a possible oxidation of the hydriodic acid formed by air is not involved. The side-reaction is accelerated by sunlight, especially in presence of ammonium molybdate. Ammonium molybdate, on the other hand, retards the reaction between chromic acid and hydriodic acid. In strongly acid solutions, ferrous salts have a negative catalytic effect; in very weakly acid solutions, the effect is positive. W. S. M.

Analysis of Zirconium Minerals and Alloys. A. TRAVERS (*Chim. et Ind.*, 1919, **2**, 385—392).—The mineral is fused with sodium peroxide, cooled, and extracted with water; zirconium oxide, titanium oxide, ferric oxide, manganese oxide, rare earths, and a portion of the silica remain insoluble, whilst silica (remainder), aluminium, and phosphoric acid pass into solution. The insoluble portion is dissolved in hydrochloric acid and treated, after neutralisation, with sodium thiosulphate; the precipitate is collected, ignited, and weighed, and allowance made for the amount of silica and titanium oxide contained in it. The former is estimated by treatment with hydrofluoric acid and the latter colorimetrically after fusion with potassium hydrogen sulphate. The iron is estimated by titration with titanium trichloride solution, manganese by the persulphate method, and rare earths by precipitation with oxalic acid. Aluminium may be estimated in zirconium-iron alloys by precipitating the zirconium and aluminium together by treatment with sodium thiosulphate after the greater part of the iron has been removed by extraction with ether, and then separating the aluminium by fusion with an alkali. [See, further, *J. Soc. Chem. Ind.*, 1919, 421A.] W. P. S.

Electro-analysis of Gold without Platinum Electrodes. J. GUZMÁN (*Anal. Fis. Quím.*, 1919, **17**, 115—120).—Preliminary analyses were carried out with an iron anode and a cathode of platinum gauze. The electrolyte was prepared by dissolving about 0.1 gram of gold in aqua regia, adding 3 grams of sodium hydroxide in 20 c.c. of water, and then 10 c.c. of freshly prepared 2% potassium cyanide solution. The electrolysis was carried out with the temperature rising to 60°, with rapid agitation of the electrolyte. Voltage, 1.9. The results obtained were excellent. A slight disintegration of the iron anode observed in this procedure was avoided by evaporation of the solution of the gold in aqua regia to remove the nitric acid. The gold was removed from the cathode by electrolysis in hydrochloric acid. Analyses with a

cathode of gilded copper gauze gave defective results. Excellent results were, however, obtained with the use of a cathode of very fine copper gauze previously nickel-plated. If the gold contains copper, it was found necessary to add 1 gram of potassium cyanide more than is required for the solution of the precipitate, and to keep the voltage below 1.9. The deposit was washed first with a dilute (2%) solution of sodium sulphite, then with water, and finally with alcohol.

W. S. M.

Determination of the Methane Content of Mine Gases or of the Concentration of a Gas in a Gaseous Mixture. FRIEDRICH KRÜGER, OTTO REINKOBER, and HANS RIEGGER (D.R.-P. 309627; from *Chem. Zentr.*, 1919, ii, 39—40).—The process depends on the property of methane of absorbing ultra-red rays. The diminution in intensity of a beam of rays caused by absorption is measured in the usual manner by means of thermocouples, bolometer, or selenium cells. The process is also applicable to other technical mixtures of gases.

H. W.

The Isolation and Characterisation of Alcohols as Allophanates. A. BÉHAL (*Compt. rend.*, 1919, 168, 945—947).—The method of preparation of the allophanates consists in passing a current of cyanic acid gas into the alcohol, filtering off the product, washing it with ether, and recrystallising the allophanate from absolute alcohol, benzene, or acetone. The alcohol is characterised by the m. p. of its allophanate, and then the alcohol is regenerated and its physical constants determined. This method can be applied to tertiary alcohols. The terpenic alcohols, except linalool, behave normally in this method, as do also the cyclic alcohols, except terpineol, unless a phenolic group is present. If the phenolic group is converted into an alkyloxy- or aryloxy-group, the reaction then proceeds normally. Alcohols having an ethenoid linking, either in the cyclic or acyclic series, give normal allophanates.

W. G.

Optical Activity and Quantitative Estimation of Menthol Dissolved in Eugenol and Phenol. OSCAR VON FRIEDRICHS (*Arch. Pharm.*, 1919, 257, 72—78).—Mixtures of menthol, eugenol, and phenol are used as local anæsthetics, particularly in dentistry, and a solution of menthol (40%), phenol (40%), and eugenol (20%) is described in the latest addition of the Swedish Pharmacopœia under the name "tinctura antidontalgica." For the estimation of the menthol content, the author has determined the specific rotation, at 18°, of solutions of menthol in phenol ($p=25-50$), in eugenol ($p=10-50$), and in mixtures of phenol and eugenol (2:1, 1:1, 1:2), and has derived formulæ by which the menthol content may be directly calculated from the optical activity.

H. W.

Use of Methylene-blue for the Detection of Sugar in Urine. LIEBERS (*Deutsch. med. Woch.*, 1916, 42, 1197; from *Bied. Zentr.*, 1919, 48, 81).—Six drops of the urine are treated

with 5 c.c. of 0.1% methylene-blue solution and ten to twenty drops of potassium hydroxide solution, and the mixture is boiled; if sugar is present in the urine, the blue colour fades, the rate at which it disappears depending on the amount of sugar. Other reducing substances in the urine do not interfere with the test.

W. P. S.

Estimation of Blood Sugar by the Modified Picric Acid Method. STANLEY R. BENEDICT (*J. Biol. Chem.*, 1919, **37**, 503—504).—It is pointed out that the final acidity of the sodium picrate-picric acid solution used for removal of the blood proteins should be about 0.05—0.04*N*. If this is not ensured, the reagent may fail to precipitate the proteins satisfactorily (compare Rohde and Sweeney, this vol., ii, 84).

J. C. D.

Estimation of Reducing Sugars Volumetrically by Schindler's Modification of Bertrand's Method. BETTINGER (*Bull. Assoc. Chim. Sucr.*, 1918, **35**, 111—113).—Bertrand's volumetric method of determining reducing sugars (*A.*, 1907, ii, 136), in which the precipitated cuprous oxide is dissolved in ferric sulphate solution and the liquid titrated with permanganate, has been rendered more rapid by using the same flask throughout and by replacing the filter-tube by a Gooch crucible. Reduction is effected in a conical flask, and the cuprous oxide washed quickly by decantation through a Gooch crucible provided with an asbestos pad, taking care to carry over as little of the precipitate as possible. Ferric sulphate solution of known titre is added to the precipitate remaining in the reduction flask, which is immediately connected by means of a rubber stopper and funnel with the Gooch crucible, and also with a tube leading to a filter-pump. A further known volume of the ferric sulphate solution is added to the Gooch crucible to dissolve the cuprous oxide remaining on the asbestos pad, and the liquid is drawn into the flask. After washing with warm water, the solution in the reduction flask is titrated with permanganate.

J. P. O.

Behaviour of Inulin in the Animal Body. Application of the Benedict Method to the Estimation of Lævulose and Inulin. RUTH E. OKEY (*J. Biol. Chem.*, 1919, **38**, 33—42).—Benedict's method for the estimation of dextrose (*A.*, 1918, ii, 247) may be applied with success to the estimation of lævulose and of inulin. It is necessary in some cases to eliminate the disturbing influence of certain salts.

J. C. D.

Estimation of Furfuroids (Furfurosans) in the Different Products of Beet-sugar Factories. II. R. GILLET (*Bull. Assoc. Chim. Sucr.*, 1918, **35**, 93—102).—In a previous paper (*A.*, 1918, ii, 248), it was shown that in the determination of pectic substances in beet-sugar factory products by the Tollens-Counciler

procedure, sucrose and hexoses in general yield a certain amount of furfuraldehyde, the quantity of which, in spite of precautions to ensure uniformity, is variable. Satisfactory results, however, are claimed to have been obtained by a preliminary elimination of the hexose sugars by fermentation, after which the liquid is distilled with hydrochloric acid and the phloroglucide precipitated and weighed in the usual manner. Operating in this way, the amount of pentosans and "pectic substances" in beet molasses, per cent. of the non-sugars present, was found to average 2.10 and 6.70 respectively. In the case of first- and second-grade sugars, the proportions were considerably higher, from which the author concludes that a large part of the so-called furfurosans or furfuraldehyde-yielding substances present in the clarified syrups are retained by the sugars when drying in the centrifugals.

J. P. O.

Filter for Use in the Estimation of Crude Fibre, etc.

F. MACH and P. LEDERLE (*Chem. Zeit.*, 1919, **43**, 251).—A disk of fine platinum gauze (16 to 17 meshes per cm., each mesh 0.5 mm. wide) is placed on a perforated porcelain plate contained in a funnel, and asbestos fibre or pulp is introduced so as to form a layer on the gauze.

W. P. S.

Systematic Extractions with Ether. JOH. PINNOW (*Zeitsch. Nahr. Genussm.*, 1919, **37**, 49—65).—At 15°, the distribution coefficient of glycollic acid between water and ether is 32, and of formic acid 2.4; at 26°, the coefficients are 38 and 2.5 respectively. The extraction of succinic acid, oxalic acid, malic acid, etc., from half-saturated solutions has been investigated. Lactic acid and citric acid may be separated and identified by extraction and use of the distribution coefficients. A substance which is not readily extracted may be estimated by making a series of successive and similar extractions; complete extraction is unnecessary.

W. P. S.

New Process for the Estimation of Oxalic Acid.

ERWIN OTT (*Ber.*, 1919, **52**, [B], 752—753. Compare H. Krause, this vol., ii, 203).—The quantitative decomposition of oxalic acid into carbon monoxide, carbon dioxide, and water by acetic anhydride in the presence of a trace of sulphuric acid had previously been described by the author (*A.*, 1913, i, 1302), and had been attributed by him to the intermediate formation of oxalic anhydride; it had not, however, been adapted by him to the rapid and exact estimation of oxalic acid and its salts.

H. W.

Recovery of Ether in Fat Estimations.

J. GROSSFELD (*Zeitsch. Nahr. Genussm.*, 1919, **37**, 81—82).—A considerable portion of the ether used in fat extractions remains in the extraction thimble; this portion of the solvent may be recovered if, as

soon as the extraction is completed, the thimble and its contents are transferred to a suitable apparatus and distilled W. P. S.

Detection of Acetone in Urine. OTTO MAYER (*Zeitsch. physiol. Chem.*, 1919, **104**, 220—228).—A general review of the methods for detecting and estimating acetone in urine. A modification of the Legal test is described which gives a reaction with acetone present in a dilution of 1:1000. J. C. D.

Nephelometric Estimation of Acetone in Urine. G. ISSOGLIO (*Giorn. Farm. Chim.*, 1917, **66**, 301—303; from *Chem. Zentr.*, 1919, ii, 150).—For the estimation of small quantities of acetone, the turbidity due to iodoform, and obtained by the use of alkaline iodine-potassium iodide solution, is compared with that given by a similarly treated solution of acetone (0.01%). The tests are performed in two similar crystallising dishes 7 cm. in diameter and 4 cm. high. Urine (100 c.c.) is mixed with half its volume of water, and 100 c.c. of the distillate are collected. The distillate (10 c.c.) is mixed with sodium hydroxide solution (5%, 10 c.c.) and water (30 c.c.), and iodine-potassium iodide solution (5%, 10% KI, 5 c.c.) is added. The turbidity obtained is compared with that simultaneously given by 10 c.c. of acetone solution (0.01%). If the acetone content of the distillate is greater than that of the control, a proportionately smaller volume is taken, which is then diluted to 10 c.c.; in the reverse case, less of the control solution is taken, but the volume of the samples must invariably be made up to 10 c.c., so that the volume of solution in the dish always amounts to 50 c.c. It is observed that the rapidity with which the turbidity appears is, within certain limits, proportional to the acetone content. H. W.

Estimation of Urea in Urine by Direct Nesslerisation. OTTO FOLIN and GUY E. YOUNGBURG (*J. Biol. Chem.*, 1919, **38**, 111—112).—The preparation of a urease product is described, the use of which permits urea nitrogen to be determined directly by Nesslerisation. J. C. D.

Rapid Method for the Estimation of Urea in Urine. JAMES B. SUMNER [with AARON BODANSKY] (*J. Biol. Chem.*, 1919, **38**, 57—61).—To 1 c.c. of urine in a centrifuge tube is added 1 c.c. of a phosphate solution and urease. The reaction is assisted by maintaining the tube warm for twenty minutes. The proteins are then removed by potassium mercury iodide and centrifugalisation, and the ammonia estimated in an aliquot part of the supernatant fluid. The method gives results which agree well with those carried out by the aeration method. J. C. D.

Estimation of Urea and Non-Protein Nitrogen in Blood and Tissue by Means of Nessler Reagent. A. GRIGAUT and FR. GUÉRIN (*J. Pharm. Chim.*, 1919, [vii], **19**, 233—243, 281—294).—From 1 to 3 c.c. of blood, serum, etc., is mixed with

2 to 6 c.c. of a suspension of 1 gram of soya-bean flour in 100 c.c. of water containing 0.4 gram of sodium dihydrogen phosphate; the mixture is kept at 56° for fifteen minutes, then treated with its own volume of 20% trichloroacetic acid, filtered, and the ammonia is estimated in the neutralised filtrate by means of Nessler reagent; the quantity of ammonia found is a measure of the urea present. To estimate non-protein nitrogen, the substance (blood, tissue, etc.) is thoroughly macerated and extracted with chloroform water, the extracts are treated with trichloroacetic acid to precipitate proteins, and, after filtration, a portion of the filtrate is digested with a mixture of phosphoric acid, three parts, and sulphuric acid, one part, and containing one-fifteenth of its volume of 10% copper sulphate solution. The ammonia formed is then estimated directly in the neutralised solution by means of Nessler reagent.

W. P. S.

Analysis of Mercury Fulminate. A. LANGHANS (*Zeitsch. anal. Chem.*, 1918, **57**, 401—445).—A method described for the estimation of mercury fulminate depends on the formation of hydroxylamine when the fulminate is dissolved in 12% hydrochloric acid; the hydroxylamine is estimated by boiling the hydrochloric acid solution with the addition of iron alum solution, and then titrating the hot mixture with *N*/20-permanganate solution. [See, further, *J. Soc. Chem. Ind.*, 1919, 389A.]

W. P. S.

Tungstic and Molybdic Complexes as Precipitants of Organic Bases. LUIS GUGLIAIELLI (*Anal. Soc. Quim. Argentina*, 1918, **6**, 57—64).—Solutions of the sodium salts of the following acids in dilute hydrochloric acid were prepared: tungstic, arsenotungstic, silicotungstic, phosphotungstic, molybdic, arsenomolybdic, phosphomolybdic, arsenotungstomolybdic, arsenovanadotungstic. The effects of these reagents on the following organic bases in dilute hydrochloric acid solution were observed and tabulated: α - and β -naphthylamine, benzidine, antipyrine, pyrimidine, caffeine, pyridine, nicotine, quinoline, cinchonine, cocaine, auramine.

W. S. M.

A Reaction of Aconitine. L. P. J. PALET (*J. Pharm. Chim.*, 1919, [vii], **19**, 295—296).—Crystallised aconitine yields a violet coloration when heated with phosphoric acid solution (D 1.7); amorphous aconitine gives a grey coloration with the test. Both forms of aconitine give a violet coloration if the phosphoric acid is mixed previously with 4% of its weight of sodium molybdate. Aspidospermine and veratrine also give a violet coloration under these conditions, but the former may be identified by the action of oxidising substances on it, and the latter by means of its reaction with mineral acids. Other alkaloids do not give a violet coloration. [See, further, *J. Soc. Chem. Ind.*, 1919, July.]

W. P. S.

Detection of the Poisons which can be Extracted with Ether from the Acid Aqueous Solution in the Stas-Otto Process. III. O. TUNMANN (*Apoth. Zeit.*, 1918, 33, 443—444, 447—448, 454—455; from *Chem. Zentr.*, 1919, ii, 42—43. Compare A., 1918, ii, 139).—*Colchicine*.—The residue, obtained according to Stas-Otto, is an amorphous, brownish-yellow mass with a very bitter taste. The sublimate is dull white or yellow and amorphous. Hydrochloric and sulphuric acids colour the sublimate yellow. The solution in sulphuric acid becomes pale green, blue, and violet on addition of a little nitric acid. Nitric acid gives a violet, greenish-yellow, and yellow coloration, which becomes red on addition of alkali. Phenol solution causes the separation of minute drops from the aqueous solution of the sublimate. Ferric chloride imparts a dark green or olive-green colour, but only dissolves the sublimate when warmed, the coloration becoming more intense.

Caffeine can be immediately sublimed from all its pharmaceutical preparations, and also from blood or urine; it is more difficult, and often not directly possible, to obtain similar sublimate from theobromine. Caffeine sublimate consists of needles and prisms with direct extinction, and six-sided platelets; theobromine sublimate never exhibits these large crystals, but is composed of needles and masses of small nodules. If the sublimate is moistened with nitric acid (5%) and a drop of silver nitrate solution (5%) is added, large, rounded nodules, from which fine, bent crystal threads project, are observed with caffeine, whilst theobromine yields large sheaves and tufts composed of long, colourless, rectangular rods, which have oblique extinction and polarise strongly in all colours. The reaction with mercuric chloride can also be applied to theobromine; the crystals of theobromine-mercuric chloride polarise in colours, generally have oblique extinction, but are composed of small groups which cannot always be recognised even with a lens. Mercuric chloride and gold chloride are not suitable reagents for distinguishing between caffeine and theobromine. With bromine-potassium bromide, crystals differing from those described by Eder (A., 1917, ii, 346) can be obtained if the caffeine sublimate is first dissolved in the bromine-bromide solution and hydrochloric acid is carefully added; in addition to a few needles (10—20 μ), single, yellow crystals separate, round which prisms gradually group themselves. All the crystals are more or less colourless after an hour. Under these conditions, theobromine does not give a precipitate. When caffeine or theobromine sublimate is treated with hydriodic acid and the solutions warmed until gas commences to be evolved, a portion of the bases collects in black lumps, whilst the remainder passes into solution; small, blackish-brown rhombs and four-sided plates separate from the caffeine solution, which appear red between crossed Nicols, show very faint pleochroism, and finally unite to irregular masses. From the theobromine solution, much larger, flat, four-sided or rhombic platelets crystallise, which show unusually marked

pleochroism and, generally, oblique extinction. Caffeine and theobromine are most readily distinguished by means of nitric acid. If the sublimates are warmed with concentrated nitric acid until a colourless rim is formed, caffeine nitrate separates in the same form as by sublimation or can be identified as chloralcaffeine, whilst the theobromine nitrate appears in short, thick crystals and rhombs which grow to masses and rosettes. The murexide test can readily be performed on an object-glass, and the results are conclusive with 20 μ g., and probably with less.

Mercuric Chloride.—To avoid confusion with the members proper of this group, the following reactions for mercury may be performed with the sublimates. Zinc chloriodide gives a pale red colour at the edges, and the precipitate is soluble in an excess of the reagent. Hydriodic acid gives a brownish-red precipitate at the rim, which is immediately soluble in excess of the reagent. Nitric acid yields a colourless solution which, on evaporation, deposits long prisms of mercuric chloride. Identification of mercuric chloride is confirmed by the following tests: Precipitation of the iodide from iodine solutions by means of copper sulphate, precipitation of the oxide by alkali, amalgamation with copper wires under a coverslip, distillation, and conversion of the distilled mercury into the iodide.

H. W.

Use of Certain Reagents for the Detection of Emetine in Human Urine. CH. MATTEI (*Compt. rend. Soc. Biol.*, 1918, **81**, 315—317; from *Chem. Zentr.*, 1919, ii, 326).—The sensitiveness of a number of reagents has been determined, using emetine solutions of known content. Tancrét's reagent gives a perceptible turbidity with 0·0000125 gram emetine hydrochloride in 5 c.c., Mayer-Valser's reagent with 0·000025 gram in 5 c.c., Dragendorff's and Bouchardat's reagents with 0·00005 gram in 5 c.c. Calcium chloride and hydrochloric acid give a distinct coloration with 0·0002 gram in 5 c.c. Froehde's reagent is also very sensitive.

H. W.

Detection of Nicotine. O. TUNMANN (*Apoth. Zeit.*, 1918, **33**, 485—486; from *Chem. Zentr.*, 1919, ii, 227).—A few crystals of *p*-dimethylaminobenzaldehyde are dissolved in a drop of fuming hydrochloric acid on an object-glass and brought into contact with a drop of an aqueous solution of nicotine. A pink, and then a reddish-violet, zone is formed at the line of contact, and the whole liquid becomes reddish-violet. The coloration increases in intensity and is permanent for ten to twenty-four hours. Under similar conditions, coniine, pyridine, and acetone do not yield colorations. Coniine, pyridine, and the other alkaloids do not influence the reaction. Aniline, in not too dilute solution, gives a red coloration, but crystals of the dye immediately separate. The reaction affords the most sensitive test for nicotine without using a microscope, and occurs within a minute with 0·2 mg. of the alkaloid. The presence of nicotine in cigar smoke is easily demonstrated in this manner.

The most sensitive microchemical reagent is a cold saturated solution of picric acid to which 10% of concentrated hydrochloric acid has been added. A yellow, amorphous precipitate, from which crystals separate in a few seconds, which is recognisable with the naked eye, is obtained with 10 μ g. nicotine. With 5 μ g. of the alkaloid, the precipitate is not formed, but the same crystals appear, generally, however, in indistinct, feathery forms, but always of the same magnitude and arranged in groups. The latter can generally be recognised by the eye, invariably with a lens. The limit of sensitiveness (in two to three minutes) is 3 μ g. The prismatic crystals shine yellow and green between crossed Nicols, and generally have oblique extinction. Aniline, coniine, and dilute pyridine do not yield crystals. Pure pyridine gives similar crystals, but not the preliminary amorphous precipitate.

H. W.

Identification of Bilirubin. E. KLAFTEN (*Wien. klin. Woch.*, 1918, **31**, 1018; from *Chem. Zentr.*, 1919, ii, 152).—Methylene-blue solution (1%, five drops) is added to the urine (5 c.c.), giving an emerald-green coloration, which disappears on addition of two to three drops of potassium permanganate solution (1%) and is replaced by an intense blue colour. The reaction is characteristic of bile pigments, and depends on their ready decomposition by potassium permanganate, whereby the yellow components are removed from the mixture of dyes.

H. W.

A System of Blood Analysis. OTTO FOLIN and HSIEN WU (*J. Biol. Chem.*, 1919, **38**, 81—110).—An attempt to combine a number of different analytical procedures into a compact system of blood analysis so that estimations of non-protein nitrogen, urea, creatinine, creatine, uric acid, and sugar may be carried out on 10 c.c. of blood. The pivotal point is the preparation of a satisfactory protein-free filtrate from the blood. For this purpose, tungstic acid was found highly satisfactory, less than 1 gram being sufficient to remove the proteins of 10 c.c. of blood. The separation is rapid and does not involve any loss of the substances which it is desired to estimate. In this filtrate, total non-protein nitrogen is determined by a slight modification of the direct Nesslerisation method (A., 1916, ii, 573). Sugar is estimated by the reduction of an alkaline copper tartrate solution, followed by the measurement of the depth of colour produced with Folin's phenol reagent (A., 1912, ii, 1012). The results indicate that this method is the most accurate of any proposed for the estimation of blood sugar.

J. C. D.

General and Physical Chemistry.

Optical Properties of Magnesium Platinocyanide. P. GAUBERT (*Bull. Soc. franç. Min.*, 1917, **40**, 177—182; from *Chem. Zentr.*, 1919, i, 509).—The author has redetermined the optical constants of magnesium platinocyanide, $\text{MgPtCy}_4 \cdot 7\text{H}_2\text{O}$, since the data recorded in the literature are discordant. The following indices of refraction are found for the usual lines: $B(687)=1.5546$, $C(653)=1.5585$, $D(589)=1.5608$, $E(527)=1.57$. H. W.

The Modifications Produced in the Spark Spectra of Different Metals by the Surrounding Medium. BOUCHETAL DE LA ROCHE (*Bull. Soc. chim.*, 1919, [iv], **25**, 305—309).—Spark spectra between metallic electrodes in oxygen or oxidising gases, such as carbon dioxide or nitrous oxide, are similar to those obtained in air and undergo the same change when a self-induction coil is introduced into the circuit. The spectra in reducing gases, such as hydrogen, illuminating gas, etc., are different, being very poor in rays, and if the self-induction coil is introduced, the metallic spectrum is still further enfeebled. This phenomenon varies in intensity with the metals examined, and the author gives the principal rays which persist in a number of metallic spectra in hydrogen or hydrocarbons. W. G.

Series Spectrum of Helium. A. LANDÉ (*Physikal. Zeitsch.*, 1919, **20**, 228—234).—A mathematical paper in which relationships between the structure of the helium spectrum and the series spectra are discussed. J. F. S.

Regularities in the Spectra of Lead and Tin. R. V. ZUMSTEIN (*Trans. Roy. Soc. Canada*, 1918, [iii], **12**, III, 59—63).—An examination of the lead spectrum shows that there are five series of three lines, the corresponding members of which have constant frequency difference, the heads of these series being the lines 7229.30, 4057.97, 3683.60, 3639.71, and 2833.17. Similarly, tin shows five groups of three lines each with constant frequency difference, the heads of each group being the lines 3801.16, 3175.12, 3009.24, 2863.41, and 2840.06. W. G.

New Lines in the Extreme Ultra-violet of certain Metals. D. S. AINSLIE and D. S. FULLER (*Trans. Roy. Soc. Canada*, 1918, [iii], **12**, III, 65—78).—The vacuum arc spectra of lead, tin, iron, nickel, cobalt, thallium, copper, aluminium, zinc, and carbon have been studied from λ 2400 to λ 1400. The vacuum arc spectra obtained for copper, zinc, and aluminium were found to correspond with the results obtained for the spark spectra. The results obtained for tin, lead, and thallium between λ 2400 and λ 1800

agree fairly well with those obtained by Saunders (compare *Astr. Phys. J.*, 1913, **43**, 234). Several new lines between $\lambda 1800$ and $\lambda 1400$ were observed and measured. W. G.

Arc Spectrum of Scandium. SIR WILLIAM CROOKES (*Proc. Roy. Soc.*, 1919, [A], **95**, 438—439).—The arc spectrum of scandium from wilkite has been photographed and the lines measured. The arc was produced between poles made by compressing a mixture of silver powder and scandium oxide. On the same plate, photographs were obtained of (i) iron, (ii) scandium and silver, and (iii) silver. In this way the silver lines were eliminated and the wave-length of the scandium lines deduced from the iron lines. A table is given containing 101 lines between $\lambda 2420.025$ and $\lambda 6305.7$. A photograph of the spectrum is reproduced in the paper.

J. F. S.

The Constitution of the Atom and the Properties of Band Spectra. H. DESLANDRES (*Compt. rend.*, 1919, **168**, 1179—1185).—Based on the formula

$$v = \pm f(n^2 p^2)(m + \alpha)^2 / 2 + B(n + \beta)^2 / 2 - C(p + \gamma)^2 / 2 \pm K$$

(compare this vol., ii, 206), the author indicates a new method for classifying band spectra. W. G.

The Absorption Spectra of the Nitric Esters of Glycerol. HARRY HEFORTH (*T.*, 1919, **115**, 840—847).

Researches on Pasteur's Principle. F. M. JAEGER (*Rec. trav. chim.*, 1919, **38**, 171—316).—This paper contains a full, detailed account of the author's crystallographic and optical researches on those complex metallic salts which can be separated into *d*- and *l*-optically active isomerides (compare *A.*, 1915, i, 867; ii, 399; 1918, i, 3, 7; this vol., i, 5, 8, 252). The salts described fall into three groups: (1) complex salts of trivalent chromium, cobalt, and rhodium with three molecules of ethylenediamine; (2) complex salts of iron, chromium, cobalt, rhodium, and iridium with three radicles of oxalic acid; (3) analogous salts of iron, chromium, and rhodium with three radicles of malonic acid. The existence of geometrical enantiomorphism in these salts is explained by Werner's octahedral distribution of the three similar bivalent radicles about the central metallic atom, and it is pointed out that, although the optically active molecules are dissymmetrical, they are not asymmetrical, but contain certain elements of symmetry, among others a three-fold axis, which sometimes also appears in the actual crystals. The optical rotatory power of these salts is often extremely high. There appears to be no direct connexion between the optical rotation and the appearance of enantiomorphous hemihedral forms on the crystals. These forms usually appear in the derivatives of oxalic and malonic acids, but rarely in those of ethylenediamine. It is concluded that the magnitude and the intensity of the rotatory power of the dissymmetrical molecules

are not dependent on chemical contrast among the substituents distributed around the central metallic atom, but that the appearance of enantiomorphous hemihedral forms is favoured by such contrast.
E. H. R.

The Phenomena of Luminescence accompanying the Oxidation of Potassium or Sodium. G. REBOUL (*Compt. rend.*, 1919, **168**, 1195—1196).—The author finds that the presence of moisture is essential to the luminescence, which really accompanies the formation of the hydroxides of the metals from the oxide.

W. G.

Cause of the Sensitiveness of Chemical Compounds to Light. JOH. PLOTNIKOW (*Chem. Zeit.*, 1919, **43**, 321—323, 337—338).—A theoretical paper in which it is shown that photochemical reactions take place according to the schemes: (i) acids, $R \cdot CO_2H \rightarrow RH + CO_2$; (ii) aldehydes, $R \cdot COH \rightarrow RH + CO$; (iii) alcohols, $R \cdot CH_2 \cdot OH \rightarrow RH + CO + H_2$; (iv) ketones, $R \cdot CO \cdot R' \rightarrow R \cdot R' + CO$; (v) diazo-compounds, $RN_2R' \rightarrow R \cdot R' + N_2$. The illumination of a double bond leads either to the production of a stereoisomeride or an intramolecular change or the formation of a saturated closed ring system. Light has the tendency to convert unsaturated systems or compounds into systems stable to light. The production of stereoisomerides or intramolecular changes is to be regarded as the first intermediate stage of the action of light. Systematic photolysis and careful choice of the source of light will effect the above-named changes in all aliphatic compounds of the types mentioned. In these changes energy may be either absorbed or evolved. If there is no possibility of the formation of a more saturated or less saturated system, then a photo-equilibrium is set up which may be displaced in either direction by varying the wave-length of the light. The photochemical and photocatalytic properties of the elements are periodic functions of their atomic weights.

J. F. S.

Limiting Absorption Frequencies of Röntgen Rays by the Heavier Elements particularly the Rare Earths. MANNE SIEGBAHN and EDV. JÖNSSON (*Physikal. Zeitsch.*, 1919, **20**, 251—256).—The limiting absorption frequency is absolutely characteristic of a chemical element, and therefore serves to identify and establish the purity of any given element. The present work was undertaken with the object of measuring this factor in the case of the rare earth metals. Various methods were available, but for various reasons were unsuitable; the methods due to de Broglie (A., 1916, ii, 509) and Wagner (*Bayr. Akad. d. Wiss.*, March, 1916) are associated with a fundamental error due to the penetration of the Röntgen rays into the crystals, whereby the reflection occurs deep in the crystal. The authors have developed a modification of this method. The light passes through a thick lead slit at the back of which the element in any of its compounds is placed;

thence the rays pass to a rock salt or calcite crystal 2 mm. thick, and are there reflected through a second slit which is fitted with gold edges, and thence through a third slit to the photographic plate. The apparatus is fitted up in a lead-lined cast-iron chamber. The Röntgen rays were produced from a glowing cathode tube. Measurements were made with the elements of atomic numbers 48—67, 78—83, 90, and 92. The following values were obtained; the atomic number is bracketed in each case: Cd (48), $\lambda=1.470$; Sn (50), $\lambda=1.537$; Te (52), $\lambda=1.606$; I (53), $\lambda=1.641$; Cs (55), $\lambda=1.706$; Ba (56), $\lambda=1.739$; La (57), $\lambda=1.772$; Ce (58), $\lambda=1.807$; Pr (59), $\lambda=1.843$; Nd (60), $\lambda=1.878$; Sa (62), $\lambda=1.948$; Eu (63), $\lambda=1.983$; Gd (64), $\lambda=2.018$; Dy (66), $\lambda=2.088$; Ho (67), $\lambda=2.125$; Pt (78), $\lambda=2.518$; Au (79), $\lambda=2.561$; Hg (80), $\lambda=2.601$; Tl (81), $\lambda=2.647$; Pb (82), $\lambda=2.687$; Bi (83), $\lambda=2.725$; Th (90), $\lambda=2.979$; and U (92), $\lambda=3.089$. The wavelengths are all given in Ångström units. The results are compared with those of de Broglie (*loc. cit.*), Wagner (*loc. cit.*), and Blake and Duane (*Phys. Rev.*, 1917).

J. F. S.

The Relation between the *L*-Series of X-Ray Spectra and the Atomic Weight. F. KIRCHOF (*Physikal. Zeitsch.*, 1919, **20**, 211—214).—The product of the *L*-wave-length into the square of the integer nearest approaching half the atomic weight (called Rutherford's ordinal number) is approximately a constant, equal to 12,550, for the elements from zinc to uranium.

F. S.

The Radioactivity of the Natural Gases of Canada. JOHN SATTERLY and J. C. MCLENNAN (*Trans. Roy. Soc. Canada*, 1918, [iii], **12**, III, 153—160).—The authors have measured the amount of radium emanation per litre of gas and the helium and nitrogen content of a considerable number of natural gases of Canada. The results show that there is no direct relationship between the radioactivity and either the helium or the nitrogen content, but that helium and nitrogen usually vary together.

W. G.

The Radioactivity of Rubidium. OTTO HAHN and MARTIN ROTHENBACH (*Physikal. Zeitsch.*, 1919, **20**, 194—202).—The β -activity of rubidium preparations of various ages since preparation show no variation such as is to be expected if the β -rays arose from a relatively short-lived isotope of rubidium, and cannot be separated or affected by chemical purification. The radioactivity appears to be an atomic property of rubidium. The radiation from a plate 25 cm. in diameter, covered uniformly with the rubidium preparation, was compared with that of uranium from a similar surface of uranium oxide of about 0.5 mg. per cm.², α -rays being absorbed by passage through 0.01 mm. of aluminium foil. The soft β -rays of uranium- X_1 , after subtracting the effect due to the penetrating β -rays of uranium- X_2 , were half absorbed in 0.015 mm.

of aluminium ($\mu_{\text{Al}}=463[\text{cm.}]^{-1}$). The β -rays of rubidium were exponentially absorbed, showing that they were homogeneous as regards velocity and penetrating power, being half-absorbed by 0.020 to 0.0225 mm. of aluminium ($\mu_{\text{Al}}=347-308[\text{cm.}]^{-1}$), and are therefore somewhat the more penetrating. The soft β -rays given by radium itself have an absorption coefficient of $312(\text{cm.})^{-1}$ in aluminium. The velocity of the rubidium rays, estimated from their absorption coefficient, is 58 to 60% of that of light.

Under the conditions described, 12.6 grams of rubidium sulphate spread over 500 cm.^2 , compared with a similar surface of 0.28 gram of uranium oxide, gave an activity per gram of rubidium salt 1/184th of that per gram of uranium oxide (total β -rays). Referred to the metals, the ratio is 1:139, and subtracting for the effect of the hard β -rays of uranium- X_2 , the ratio is 1:32. By using less and less rubidium salt and extrapolating to a film of zero thickness, the ratio is further increased in favour of the rubidium to 1:15, to an accuracy of 20%. That is, the β -activity of rubidium is 1/15th of that due to uranium- X_1 in the same weight of uranium, absorption in the material being corrected for. For thorium, the ratio is probably 1/10th, comparing similar β -rays.

Applying the law of radioactive change, the product of rubidium should be an isotope of strontium, and of potassium an isotope of calcium. The investigation of the atomic weight of calcium derived from potash felspar, containing only small amounts of calcium, is suggested, as if the calcium is a product of the potassium, its atomic weight should be about a unit less than the accepted value. The period of half-change of rubidium, calculated from the ratio of its β -activity to that of uranium- X_1 , is about 10^{11} years, and for potassium probably three times as great. If the age of the oldest felspars is taken as 10^9 years, only 0.17% of the potassium should have changed into calcium. The period of potassium, however, may be as great as seven times that of rubidium, and it is doubtful if the expected difference of atomic weight would be detectable. Similarly for the possible case of caesium transforming itself into barium, though no β -activity of caesium has been detected, an examination of the caesium mineral pollux is suggested. F. S.

Is the Electrical Conductivity of the Elements Conditioned by the Presence of Isotopes? F. H. LORING (*Chem. News*, 1919, 119, 14—16).—Assuming that those elements the atomic weights of which are not whole numbers are mixtures of two isotopes the atomic weights of which are whole numbers, it is suggested that the proportions of the two isotopes in the element may determine its electrical conductivity. It is further suggested that in those elements having a high conductivity there may be a greater proportion of the isotope of lower atomic weight, whilst in the non-conducting elements the proportions may be reversed. This idea is developed in a table, in which, for a number of conducting and non-conducting elements, the atomic weights and proportions of hypothetical isotopes are given. E. H. R.

New Process for Measuring the Specific Inductive Power of Liquids. FÉLIX MICHAUD and AHMED BALLOUL (*Ann. Physique*, 1919, [ix], 11, 295—322).—The apparatus consists of a cylindrical condenser with a vertical axis, between the armatures of which the liquid rises under the action of the electric field, this rise being shown by a lowering of the level of the liquid in a lateral glass tube. The specific inductive powers of benzene, vaselin, *cyclohexane*, and turpentine were measured by this method, the results for benzene being 2.28 and for *cyclohexane* 1.87. Solutions of phenol in benzene were also examined, and it was found that the dielectric constant reaches a maximum at a concentration of 11% of phenol. With mixtures, the phenomenon of "electro-osmosis" may occur, and it is proposed to study this in detail. The apparatus, slightly modified, may be used as an electrometer.

W. G.

Characteristics of the Spark Discharge and its Effect in Igniting Explosive Mixtures. CLIFFORD C. PATERSON and NORMAN CAMPBELL (*Proc. Physical Soc. London*, 1919, 31, 168—228).—The object of the work described in the paper was to determine the relationship between the electrical characteristics of a spark discharge and its power of igniting explosive mixtures. An attempt was made to produce a form of discharge in which the current and the duration of the discharge could be controlled and varied. This failed; the discharges obtained always consisted of a discontinuous series of individual sparks, each of which lasted for a time which could not be subdivided. Quantitative measurements show that each of these individual sparks consists in the passage of a definite quantity of electricity, Q , across the gap, and represents the discharge of a condenser of definite capacity previously charged to the spark potential of the gap. The maximum duration of a spark is of the order 0.00005 second, but there is reason to believe that the actual value is considerably less than this figure. It was found impossible to obtain a discharge which was continuous, except when it took the form of an arc or a brush. The sparks obtained from an induction coil are of the same type as those obtained from a condenser. It is therefore suggested that the quantity Q , together with the form of the spark gap, may be sufficient to define the nature of the spark and to determine its igniting power. It is shown that discharges which consist of a series of similar sparks have the same igniting power as a single spark of the same character; that is to say that the ignition, if it occurs at all, occurs at the first spark. Working with mixtures of petrol and air, it is shown that the igniting power of a spark increases with both the capacity discharging and the spark potential, but varies much more rapidly with the latter factor. The energy required for ignition decreases rapidly as the spark potential increases, and there is no indication that, if the spark potential were sufficiently increased, the energy required for ignition might not be reduced greatly beyond the measured limit, namely, 0.0004 joule. Other things

being equal, electrodes with small radius of curvature have greater igniting power; the metal of which the electrodes is made is of no importance from the point of view of ignition. J. F. S.

The State of Super-conductivity in Metals. C. A. CROMMELIN (*Chem. Weekblad*, 1919, **16**, 640—669).—A lecture delivered before the Natuurkundig Gezelschap in Leiden. Special reference is made to the work of Kamerlingh Onnes. W. S. M.

Electromotive Activity of Carbon Monoxide. II. K. A. HOFMANN and B. WURTHMANN (*Ber.*, 1919, **52**, [B], 1185—1194).—It has been previously shown (this vol., ii, 8) that the oxidation energy of carbon monoxide at the ordinary temperature can be largely converted into electrical energy when the carbon monoxide is oxidised at a copper electrode wetted with alkali hydroxide solution which is connected with a copper or platinum-air electrode. It is now shown that, in contrast to hydrogen, the activity of carbon monoxide is 0.12 volt greater at a copper than at a hydrogen electrode, and, further, that the potential developed by the oxidation of carbon monoxide is greater than that developed from hydrogen by 0.3 to 0.08 volt. A copper electrode is particularly useful in the utilisation of air in the carbon monoxide cell, since it forms a primary oxide with the oxygen the oxidative power of which is more than 0.2 volt greater than that of cupric oxide.

The potentials of the following cells are recorded, the electrolyte being 15% pure potassium hydroxide solution in every case: $H_2|Pt$, electrolyte, $HgO|Hg$, 0.93 volt at 22°; $CO|Pt$, electrolyte, $HgO|Hg$, 0.91 volt; $CO|coppered\ carbon$, electrolyte, $HgO|Hg$, 0.96 volt at 17—18°; $CO|coppered\ carbon$, electrolyte, $Pb|air$, 1.17 volt at 14°; $CO|platinised\ carbon$, electrolyte, $Pt|air$, 1.05 volt at 18°; $CO|Cu$, electrolyte, $copper\ oxide|air$, 0.95—0.99 volt at 20°; $CO|platinised\ platinum$, electrolyte, $copper\ oxide|air$, 0.91 volt at 18°; $H_2|platinised\ platinum$, electrolyte, $copper\ oxide|air$, 0.958 volt at 18.3°. H. W.

Methods of Measuring Electric Cataphoresis. THE. SVEDBERG and HUGO ANDERSSON (*Kolloid Zeitsch.*, 1919, **24**, 156—165).—The various methods which have been used for measuring the migration velocity of colloidal particles in an electric field are critically discussed and their errors enumerated. It is held that none of the methods hitherto described is entirely satisfactory, although that due to Linder and Pieton (*T.*, 1897, **71**, 568) is usable in some circumstances. The authors describe the construction of a small vessel in which microscopic cataphoresis experiments may be carried out with either direct or alternating current. A photomicrographic method is described by which cataphoresis may be measured by means of a direct current flowing for very short periods. A microscopic method is also described in which alternating current is used. A comparison of the results obtained by these methods shows that the latter is more exact and gives values

which more nearly agree with the theoretical values than the former.

J. F. S.

Some Determinations of the Heat Conductivity of Selenium. EDNA D. SAYCE (*J. Proc. Roy. Soc. N.S. Wales*, 1917, **51**, 356—363).—It was found that the thermal conductivity of selenium varied over a wide range, and was affected by the conditions which influence its electrical conductivity, and in the same direction, but in general to a slighter extent. The thermal conductivity of vitreous selenium at 25° was found to lie between 0·000293 and 0·000328. That of crystalline selenium at 25° varied from 0·00070 to 0·00183. The values for the crystalline form increased in general with the temperature of preparation, but diminished with age. In all the cases examined, the temperature-coefficient was positive. All measurements were made with the selenium in darkness.

W. G.

The Determination of the Melting Points of Fats and Similar Substances by Means of the "Ascension" Method.

D. J. DE JONG (*Pharm. Weekblad*, 1919, **56**, 925—931).—A short column of fat is allowed to solidify for twenty-four hours in a narrow glass tube open at both ends. The tube is placed vertically in water or glycerol so that the top of the fat column is below the level of the liquid. The temperature of the bath is raised slowly until the melting point is reached, at which temperature the column of fat begins to rise in the tube. Constant results were obtained when a thin-walled tube of 1 mm. internal diameter was used with a fat column 1 cm. long placed 1 cm. below the surface of the water.

W. S. M.

The Freezing Point of Solutions with Special Reference to Solutions Containing Several Solutes. CHARLES EDWARD FAWSITT (*T.*, 1919, **115**, 790—801).

Cryoscopy in Acetylene Tetrabromide. R. LESPIEAU (*Compt. rend.*, 1919, **169**, 31—32).—Using benzene, chloroform, carbon tetrachloride, and ethyl ether as solutes, the author finds that the cryoscopic constant of acetylene tetrabromide, m. p. 0—0·13°, is 217, and that it varies but little with the nature of the dissolved substance or the concentration providing that the solution remains dilute.

W. G.

Variation of the Vapour Pressure with the Temperature.

C. EMILIO CARBONELLI (*Gazzetta*, 1919, **49**, i, 151—153).—If θ denotes the absolute critical temperature of any liquid, π its critical pressure, and f its vapour pressure at a temperature T lying between absolute zero and the critical temperature, results in close agreement with the experimental data are given by the formula $\lg \pi/f = (\theta - T)/T \cdot \lg h\theta/T$, h being a constant characteristic for each liquid. The values of $\lg h$ are: for carbon disulphide,

2·21503; chloroform, 2·58134; alcohol, 3·6765; water, 2·92714; ethyl ether, 2·80416; benzene, 2·64664; sulphur dioxide, 2·79064; cyanogen, 2·92481; and ammonia, 2·79. T. H. P.

Maximum Vapour Pressures of Benzene and cycloHexane at Moderate Temperatures and Calculation of their Principal Specific Heats. C. DÉJARDIN (*Ann. Physique.*, 1919, [ix], 11, 253—291).—A more detailed account of work already published (see this vol., ii, 95). W. G.

The Saturated Vapour Pressures and the Heats of Vaporisation of Propyl Acetate at Different Temperatures. E. ARIÈS (*Compt. rend.*, 1919, 168, 1188—1192).—Using the formula previously given (compare A., 1918, ii, 352) for calculating the value of the function Γ , from these results the author has calculated the saturated vapour pressures and heats of vaporisation of propyl acetate at different temperatures, and finds that the calculated values are in close agreement with those observed by Young. W. G.

Volatility. OTTO RUFF (*Ber.*, 1919, 52, [B], 1223—1238).—A theoretical paper in which the boiling point of the substance under atmospheric pressure is treated as a measure of its volatility. A series of tables is given showing the b. p. of fluorides, chlorides, hydrides, nitrides, and oxides as far as these have been determined. A discussion is then entered on with regard to the part played by mass, atomic volume, number of atoms in the molecule, negative minimal loading of the atoms in the molecule, and molecular symmetry on volatility. For details, the original paper must be consulted. H. W.

Thermochemistry of Organic Fluorine Compounds. FRÉDÉRIC SWARTS (*J. Chim. Phys.*, 1919, 17, 3—70).—Using a Langbein calorimetric bomb in which the silica-containing parts have been replaced by platinum, the author has determined the heat of combustion of a very large number of organic fluorine compounds. The results are recorded as (i) heat of combustion per gram, (ii) molecular heat of combustion (a) at constant pressure and (b) at constant volume. The heat of formation is also calculated in each case. The method of preparation, density, freezing point, and boiling point are recorded for every compound. By comparing the present results with those of Berthelot for other substances, the heat of substitution of one atom of fluorine for one atom of hydrogen is calculated. The substitution of the first atom of fluorine for hydrogen increases the heat of formation by about 17 cal., although the value fluctuates considerably for the various types of compounds; the introduction of the second atom of fluorine increases the heat of formation more than the first in all cases. The effect of substituting fluorine in benzene derivatives is also studied. It is shown that the replacement of one hydrogen

atom by fluorine increases the heat of formation by 15·8 cal., but the second further increases it by 22·3 cal. if the second atom enters the para-position. The substitution of fluorine in mono-substituted benzenes increases the heat of formation from 8·15 cal. in the case of *o*-fluoronitrobenzene to 22·6 cal. in the case of *m*-fluorophenol. Similar calculations are made for tri- and tetra substitution products of benzene. J. F. S.

Heat of Coagulation. H. R. KRUYT and JAC. VAN DER SPEK (*Kolloid Zeitsch.*, 1919, **24**, 145—155).—The heat change occasioned by the sudden coagulation of arsenic sulphide sol and ferric oxide sol has been determined. In the case of arsenic sulphide, the coagulation was brought about by the addition of a solution of alum or potassium chloride. In all experiments, the heat change was extremely small, the amount of heat developed being 0·01—0·05 gram cal. per gram of arsenic sulphide. Ferric oxide sols were coagulated by the addition of sodium sulphate solution, and in this case the heat developed was considerably greater, amounting to 2 gram cal. per gram of ferric oxide. Experiments show that the heat developed depends very largely on the chlorine content of the sols. It is in keeping with expectation that there should be a considerable difference in the development of heat in the two cases, for the coagulation of ferric oxide sol is accompanied by a considerable increase in volume, whilst that of arsenic sulphide is accompanied by a very small diminution in volume. Further experiments were made to determine the heat change brought about by the adsorption of crystal-violet by animal charcoal. The results are only approximate and give the order of magnitude of the change; thus 5 grams of charcoal adsorb 2·21 millimols of crystal-violet with a heat absorption of 16·58 gram cal. For calculations of the amount of energy set free in the coagulation of arsenic sulphide sol, compare Linder and Picton (*T.*, 1892, **61**, 114). J. F. S.

Calculation of the Divergences from Avogadro's Law by the Method of Compressibilities. Application to Hydrogen Bromide. PH. A. GUYE (*J. Chim. Phys.*, 1919, **17**, 141—170).—A theoretical paper in which it is shown that the work of Moles (*A.*, 1916, ii, 42, 526) and Reiman (*A.*, 1917, ii, 137, 200) on the density of hydrogen bromide definitely indicates that the compressibility (pv) of this gas at 0° and at pressures above 1 atm. is not a linear function of the pressure (p) nor of the inverse of the volume ($1/v$). This being the case, the product pv ought to be represented by a formula of the second degree of p or $1/v$, and this equation ought to hold for all gases less volatile than carbon dioxide. By means of the modified van der Waals's equation, it is known at once whether a gas ought to be represented in the neighbourhood of 1 atm. by an equation of the first or second degree. The use of a formula of the second degree, $(pv) = 1 + \alpha + ap + bp^2$, or $(pv) = 1 + \alpha' + \alpha'/v + b'/v^2$ for the extra-

polation of the limiting value $(pv)_0$ which enters into the expression, giving the divergences from Avogadro's law, is justified by consideration of the best established equations of state. Two methods are indicated for calculating the constants of the preceding equations, and when these are applied to the results of Moles and Reiman (*loc. cit.*), the following values are obtained for hydrogen bromide at 0° : (i) divergence from the law of Avogadro: $(1 + \lambda) = (pv)_0 / (pv)_1 = 1.00934$; (ii) divergence of the compressibility between 0 and 1 atm.: $A'_0 = 0.00925$. The experiments of Moles and Reiman lead to the same results. The methods adopted in these calculations are discussed at some length in the paper.

J. F. S.

Investigation of Poisson's Ratio by Means of the Gaseous Volume and Specific Heat at Low Temperatures.

RUDOLF MEWES (*Zeitsch. Sauerstoff Stickstoff Ind.*, 1918, **10**, 93; from *Chem. Zentr.*, 1919, i, 505).—A formula has previously been developed whereby the specific volumes of gases can be estimated from observation on the specific heats $k = c_p / c_v$ and c_p at low temperatures. The ratio v_{15}/v_t and v_0/v_t has been calculated from the formulæ $v_{15}/v_t = (1 + \alpha)^{-t}$ and

$$v_{15}/v_t = v_{15} / [At(c_p - c_v/k) / P + v_{15}]$$

and introduced into Poisson's equation. Since the calculated and experimental results are not in harmony, Poisson's equation does not appear to hold good.

H. W.

Gaseous Volumes at Low Temperatures. RUDOLF MEWES (*Zeitsch. Sauerstoff Stickstoff Ind.*, 1918, **10**, 81—82; from *Chem. Zentr.*, 1919, i, 505).—Theoretical considerations based on a table which gives the necessary data for helium, hydrogen, nitrogen, oxygen, air free from carbon dioxide and carbon monoxide, show that Gay-Lussac's law is not approximately obeyed at low temperatures (at about -192°), and that the most accurate observations yet made are vitiated by some error which is not yet explained.

H. W.

Modification of Victor Meyer's Vapour Density Apparatus.

GIOVANNI ROMEO (*Gazzetta*, 1919, **49**, i, 172—174).—In this apparatus, the upper, narrow, tubular part above the bulb in which the substance is vaporised is considerably shortened, and round it is wrapped, in the form of a spiral, the tube through which the displaced air passes to the graduated measuring tube. The lower end of this spiral tube is connected with the top of the bulb, whilst the upper end emerges through the stopper of the jacket containing the heating vapour. In this manner, the apparatus is made shorter and more easily manipulated, less time is required for the uniform heating of the apparatus, and condensation of the vaporised substance on the cool parts of the apparatus is entirely avoided.

T. H. P.

The Adsorption of Helium by Charcoal. STUART McLEAN (*Trans. Roy. Soc. Canada*, 1918, [iii], **12**, III, 79—81).—A very

small amount of helium is adsorbed by charcoal at the temperature of liquid air, the amount adsorbed being apparently independent of the volume of helium introduced into the apparatus. W. G.

An Apparatus for Studying the Dissociation of Carbonate Rocks. G. A. BOLE (*J. Amer. Ceram. Soc.*, 1919, 2, 410—417).

—The dissociation of carbonate rocks may be studied by heating 0.1 gram of the sample in a modification of Victor Meyer's vapour density apparatus, consisting of a small platinum bucket which fits over the lower end of the porcelain sheath of a thermocouple and is held in place by a small porcelain wedge. The thermocouple is then placed in a tube of fused silica, 25 cm. long and 1.25 cm. in diameter, provided with a side-tube leading to a pneumatic trough and gas burette. The top of the silica tube is closed with a ground-glass stopper, into which are fused the wires of the thermocouple. The stopper also contains a glass tube carrying a stopcock. The lower part of the silica tube is surrounded by an electric furnace. The temperature of the sample is raised to about 450°, with the stopcock open to expel any moisture. The stopcock is then closed, the temperature raised steadily, and the volume of gas evolved is measured at regular intervals of time until the dissociation is complete. The gas is examined for carbon monoxide, and, if this is found, a fresh portion of the sample is treated for removal of organic matter, and a fresh determination of the dissociation temperature is then made. It is necessary to make a blank test in order to ascertain the expansion of the air in the apparatus at various temperatures and to correct the volume of gas accordingly. The same apparatus may be used for determining the temperature at which the dissociation pressure is just above that of the atmosphere by maintaining it at the highest temperature at which gas is evolved. In determining the rate of dissociation, 0.5 gram of the sample is placed in a small platinum bucket in the neck of the apparatus, the silica tube is heated to about 50° above the temperature at which the determination is to be made, the temperature allowed to fall slowly to the desired temperature and maintained constant for about fifteen minutes. The bucket is then released and allowed to fall to the bottom of the tube, and the gas evolved is measured after a definite interval of time. A series of determinations is made at increasingly higher temperatures, and the results are plotted. The apparatus may also be used to determine the carbon dioxide associated with lime and magnesia respectively in limestone and dolomite by raising the temperature to 750° while the sample is in the neck of the tube, then releasing the bucket, raising the temperature to 900°, and measuring the gas evolved at each temperature. The apparatus is simple, easy to use, rapid, and accurate. Organic matter, occluded gases, and moisture may be driven off by manipulating the stopcock immediately before making a determination. A. B. S.

Piezo-chemical Studies. XV. Experimental Proof of Braun's Law. ERNEST COHEN and A. L. TH. MOESVELD (*Zeitsch. physikal. Chem.*, 1919, **93**, 385—515. Compare A., 1917, ii, 566).

—With the object of ascertaining experimentally the extent to which Braun's law is true, the authors have determined (i) the temperature-coefficient of the solubility of *m*-dinitrobenzene in ethyl acetate, (ii) the pressure-coefficient of the solubility, (iii) the fictitious volume change, and (iv) the fictitious heat of solution of the same pair of substances (see A., 1918, ii, 297). These values when obtained were substituted in the expression

$$(dx/d\pi)_T : (dx/dT)_\pi = -T\Delta V/Q,$$

and the value of Q obtained and compared with the experimentally determined value of Q . In the expression above, $(dx/d\pi)_T$ is the pressure-coefficient of the solubility at constant temperature, $(dx/dT)_\pi$ the temperature-coefficient of the solubility at constant pressure, ΔV the fictitious volume change, that is, the volume change when a fixed amount of substance dissolves in an infinitely large volume of solvent at the temperature T , and Q the fictitious heat of solution. The value of Q found by this equation is 21.07 ± 0.10 gram cal./gram, whereas the experimental value of Q is 21.02 ± 0.02 gram cal./gram. From these figures, it is concluded the Braun law holds within the limits of experimental error. The solubility of *m*-dinitrobenzene in 100 grams of ethyl acetate is found to be 21.80 grams at 0.02° , 23.35 at 2.48° , 24.92 at 5.00° , 26.62 at 7.50° , 28.55 at 10.00° , 30.66 at 12.50° , 32.95 at 15.00° , 35.45 at 17.50° , 38.20 at 20.00° , 41.20 at 22.50° , 44.60 at 25.00° , 48.38 at 27.50° , 52.53 at 30.00° , 57.24 at 32.50° , and 62.32 at 35.00° . Calculating from these figures, the temperature-coefficient at 30.00° is found to be 0.5653 ± 0.0007 gram mols. per 100 mols. of solution per degree, or 0.755 ± 0.001 gram per 100 grams of solution per degree. An apparatus is described whereby the solubility under various pressures may be determined. Using this apparatus, the solubility of *m*-dinitrobenzene in ethyl acetate is determined at 30° under pressures 0, 100, 220, 300, 380, and 480 atmospheres, and from the results the pressure-coefficient of the solubility calculated to $(dx/d\pi)_{\pi=1} = -0.00867 \pm 0.00003$ mol. %/per atm., or, if c = weight %, $(dc/d\pi)_{\pi=1} = -0.01161 \pm 0.00005$ weight %/per atm. The specific volume of various solutions of *m*-dinitrobenzene in ethyl acetate has been determined at temperatures between 20.00° and 30.00° by means of an Ostwald-Sprengel pycnometer, and also by a dilatometric method. From the results, it is shown that $v_c = 0.96978$, that is, the specific volume of a solution saturated at 30.00° and 1 atm. pressure. The specific volume of solid *m*-dinitrobenzene at 30.00° was determined by a dilatometric method, using water as the liquid, and the value 0.63872 found. From the data thus accumulated, the fictitious volume change is calculated, and the values 0.0442 ± 0.0001 c.c./gram and 7.392 ± 0.15 c.c./mol. obtained. A long description of the method of experimentally obtaining the fictitious heat of solution is given, and from the experiments the value 21.02 ± 0.025 gram cal./per

gram, or 3534 ± 5 gram cal./per mol., obtained. The paper ends with a long and detailed criticism of a paper on the same subject by H. F. Sill (A., 1917, ii, 75). J. F. S.

Liquid Crystals and Anisotropic Liquids. D. VORLÄNDER (*Zeitsch. physikal. Chem.*, 1919, **93**, 516—520).—Polemical against Baur (*Jahrb. Chem.*, 1916, **25**, 362), Bose (A., 1907, ii, 443; 1908, ii, 1017), Nernst (*Lehrb. theoret. Chem.*), and Herz (*Moderne Probleme allgem. Chem.*). The author protests against the views put forward by the authors named, that liquid crystals are heterogeneous substances consisting of a disperse phase and a dispersion medium. J. F. S.

Orientation of Anisotropic Liquids on Contact with Crystals. II. F. GRANDJEAN (*Bull. Soc. franc. Min.*, 1917, **40**, 69—105; from *Chem. Zentr.*, 1919, i, 498—499. Compare A., 1917, ii, 451).—The author describes the behaviour of the same crystals which were previously used with five new anisotropic liquids, *p*-azoxyanisolephenetole, dibenzylidenebenzidine, *p*-ditolylidenebenzidine, methoxycinnamic acid, and *p*-anisylideneaminoazotoluene. Orientation occurs in ninety cases out of a hundred, and hence is a general property. The crystal surface causes a peculiar field of force, the nature of which is not explained. It orientates anisotropic liquids in such a manner that their axes can assume one or more definite positions, which are termed equilibrium or field directions. One of these is perpendicular to the face of the crystal. If the latter corresponds with a net plane of high density, there is generally one or more of these directions parallel to the face. With respect to behaviour on change of temperature, three types are to be considered, in which (i) the orientation is not greatly altered, (ii) a well-defined orientation suddenly passes into a second arrangement, and (iii) the orientation changes gradually with changing temperature. H. W.

Periodic Precipitation. (Miss) A. W. FOSTER (*Trans. Roy. Soc. Canada*, 1918, [iii], **12**, III, 55—57).—The addition of one drop of a 1% solution of silver nitrate to a thin sheet of gelatin impregnated with potassium chromate produced precipitation in the form of Leisegang's rings. When a colloidal copper solution was used instead of water for making the gelatin plate, the precipitate was not in the form of rings, but as microscopic quantities scattered over the plate. Similar experiments were performed, agar being used instead of gelatin, and it was found that in this case the presence of the positively charged copper particles did not change the character of the precipitate. W. G.

Rhythmic Solidification. D. VORLÄNDER and ILSE ERNST (*Zeitsch. physikal. Chem.*, 1919, **93**, 521—526).—Solutions on evaporation in many cases deposit crystals in a rhythmic manner. This phenomenon is particularly well observed in the crystallisation of an aqueous solution of 5-nitrophenyl-2-glycine-1-carboxylic acid;

this substance crystallises in open vessels in a series of rings, the formation of which is connected with the surface tension and the adhesion of the solution on the vessel walls, and is also due to the fact that after the deposition of the first crystals the solution is drawn by capillary attraction to the crystals. As the evaporation proceeds, the surface tension of the solution overpowers the adhesion and capillary attraction, so that the solution withdraws itself spasmodically from the edges of the dish. In the case of molten substances, the authors have found very few substances which solidify rhythmically, but this phenomenon is well shown by the ethyl ester of *p*-ethoxybenzylideneaminophenylpropionic acid. This substance, which was prepared by the method described by Beilstein and Kuhlberg (*Annalen*, 1872, **163**, 162), melts at 59° to an amorphous liquid; on supercooling the molten substance to 34°, it forms liquid crystals. The rhythmic solidification occurs when either of the liquid forms passes into the crystalline solid, and takes place as follows: When a few drops of the molten substance are placed on a clean glass plate, a small, round, crystalline mass first forms; this exerts a capillary attraction on the surrounding liquid, and the liquid rises in the crystal mass and solidifies on top of it, and also on the sides, whilst the level of the liquid falls. Then a period of no growth of the crystal height sets in, because the adhesion of the liquid to the glass plate has overpowered the capillary attraction, but at the same time the crystal mass begins to grow rapidly from the sides until a quantity of liquid is held in the crystal network, when the side growth ceases and the vertical growth recommences. These three processes then repeat themselves in the same order. Photomicrographs illustrating the crystallisation in this case are appended to the paper.

J. F. S.

New Method of Weighing Colloidal Particles. E. F. BURTON (*Proc. Roy. Soc.*, 1919, [A], **95**, 480—483).—A preliminary paper in which it is shown that by superimposing on a colloidal particle the motion produced by an electrical field on that produced by gravitation, colloidal solutions which possess particles too small to settle under the influence of gravity alone may be made to settle. The experimental procedure consists in superimposing on a colloidal solution contained in a migration tube a small column of conductivity water of the same specific conductivity as the colloidal solution. The position of the interface between the two liquids is noted, and a current of *E.M.F.* ca. 100 volts is passed for ten minutes, reversed, and again passed for ten minutes. The position of the interface is noted at the moment of reversal and at the end of the experiment. In the first period of ten minutes, the motion of the particles is due to a force $Xe + mg$ and in the second ten minutes to $Xe - mg$. From these values, the equation $a^2 = 9/2 \cdot nv/(\rho - \rho^1)g$ is deduced, in which a is the radius of the particle, v the velocity under the influence of gravitation, ρ and ρ^1 the densities of the particle and medium respectively, n the viscosity of the solution, and g the gravitational force. By

this method, colloidal particles of silver were found to have a radius 2.2×10^{-5} cm., whereas 1.7×10^{-5} was obtained by the counting method. The velocity v was 8.3×10^{-5} cm. per sec.

J. F. S.

Colours of Colloids. V. Metallic and Vitreous Lustre.

WILDER D. BANCROFT (*J. Physical Chem.*, 1919, **23**, 289—347).—A continuance of the discussion on colour phenomena dealt with in previous papers (A., 1918, ii, 102; this vol., ii, 187, 275). In the present paper, metallic and vitreous lustre as it affects colour is discussed in connexion with minerals, feathers, and beetles.

J. F. S.

Emulsification of Water and of Ammonium Chloride Solutions by Means of Lamp Black.

WILLIAM C. MOORE (*J. Amer. Chem. Soc.*, 1919, **41**, 940—946).—Weighed quantities of lamp black, both the commercial article and that previously extracted with benzene, were stirred for measured times with petroleum (D¹⁵ 0.8149) and water or solutions of ammonium chloride of known concentration. The emulsions thus obtained, in which petroleum was the continuous phase, were examined under a micrometer microscope, and the diameter of the aqueous drops measured. The experiments show that various samples of lamp black have widely differing emulsifying properties. With a large quantity of lamp black, smaller emulsified drops of water are obtained in petroleum than when less lamp black is used. Water wets commercial lamp black less readily than the extracted lamp black. Ammonium chloride in normal solution wets the commercial lamp black more readily than the purified substance. Water wets purified lamp black more readily than does ammonium chloride solution, the converse being the case for the commercial lamp black. The drops of emulsified water become larger the greater the concentration of the ammonium chloride, owing to the increasing surface tension of the ammonium chloride solution. The effect of changing the time of stirring is somewhat indefinite; a tendency is shown for the size of the drops to pass through a minimum as the time is increased.

J. F. S.

Electromagnetic Hypothesis of the Kinetics of Heterogeneous Equilibrium, the Structure of Liquids and Cohesion.

WILLIAM D. HARKINS and H. H. KING (*J. Amer. Chem. Soc.*, 1919, **41**, 970—992).—A theoretical paper in which an hypothesis is developed that the distribution of a solute between various phases and interfaces is conditioned by the intermolecular electromagnetic fields. Cohesion is considered to be due to these fields, and is explained on the basis of the valency theory of Lewis (A., 1916, ii, 310) as being due to intermolecular fitting of electrons in the outer shells of atoms. The constant surface film of butyric acid on the surface of water is found to contain 2.78×10^{14} molecules, whilst if benzene covers the water phase, the layer contains

2.79×10^{14} molecules per sq. cm. Thus the presence of benzene does not affect the number of molecules in the film. A theory of solubility and of thermodynamic environment is developed, and an hypothesis is made to explain the variation of the fugacity or thermodynamic potential of a component, with variations in its environment. In this connexion, solubility, Raoult's law, melting point, compressibility, coefficient of expansion, latent heat of vaporisation, adsorption, and surface structure are discussed. The theory is complicated, and the original should be consulted for details.

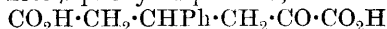
J. F. S.

Chemical Affinity. FRITZ EPHRAIM (*Naturwiss.*, 1919, 7, 49—55; from *Chem. Zentr.*, 1919, i, 409—410).—The energy of a reaction is, in general, the sum of the energies of a number of component reactions, and therefore gives little information about the latter. The energy of analogous reactions is best studied with closely related compounds, whereby the common side-reactions are most readily eliminated. In this manner, the relative affinity of water of crystallisation to different molecules is conveniently determined by investigation of substances such as the alums. Studies of this nature are best effected by estimation of the affinities of subsidiary valencies with hydrates, and particularly ammoniates. The gaseous nature of ammonia allows the thermochemical investigation to be replaced by determination of the dissociation temperature, that is, the temperature at which the pressure of ammonia is equal to the atmospheric pressure. The affinity of ammonia for the molecule in question is obviously greater as the dissociation temperature is higher. The following compounds have been compared in this manner: $\text{NiI}_2 \cdot 6\text{NH}_3$, $\text{CoI}_2 \cdot 6\text{NH}_3$, $\text{FeI}_2 \cdot 6\text{NH}_3$, $\text{MnI}_2 \cdot 6\text{NH}_3$, $\text{ZnI}_2 \cdot 6\text{NH}_3$, $\text{CdI}_2 \cdot 6\text{NH}_3$. The temperature of decomposition decreases with increasing atomic volume, and the product of dissociation temperature and atomic volume is approximately constant. Consequently, the dissociation temperature can be calculated if that of a similar substance and the atomic volume of the metal are known, and, conversely, unknown atomic volumes can be calculated from the observed dissociation temperature. Irregularities are only observed with cadmium. When compounds of a metal with different acid radicles are investigated, the size of the latter appears to be important, but its effect can only be estimated with difficulty, since, in complex radicles, only that portion which is closely related to the metallic atom should be considered. The affinity for neutral molecules is particularly marked with large acid radicles. The relationships are most favourable when the metal is surrounded by acid radicles, as in the case of a multivalent metal united to several univalent radicles. With increase in volume of the neutral molecules, as with transition from ammonia to alkylamines, the affinity decreases. With complex cations, the neutral portion is more firmly bound as the size of the metal decreases. Conversely, the stability of complex ions increases with increasing volume of the metal. Systematic investigation of the

stability of a group of complex compounds permits the decision as to whether the complex is united to the anion or cation, and thus allows a determination of constitution in solid substances. The method is, in principle, applicable to all dissociable compounds. From this point of view, an explanation is given of the fact that the capacity of neutral salts to cause the separation of amino-acids is reversed by addition of traces of acid or alkali. The formation of dissociation equilibria is in many respects analogous to the evaporation of a liquid. The absolute boiling points under the same pressure of chemically related substances stand to one another in a constant ratio. The boiling-point rule can also be used as dissociation rule, as is shown in the case of the amines of the iodides previously described. The rule is also true for substances of widely differing chemical nature. The calculation of the dissociation temperature for any pressure is therefore possible when it is known at any definite pressure. The limits of existence of compounds can therefore be defined.

H. W.

Fission of Acid Salts in Aqueous Solution into Normal Salts and Free Acids. W. DIECKMANN and ALBIN HARDT (*Ber.*, 1919, 52, [B], 1134—1142. Compare Thoms and Sabalitschka, *A.*, 1917, i, 700; Sabalitschka, this vol., ii, 282; McCoy, *A.*, 1908, ii, 466; McCoy and Chandler, *A.*, 1908, ii, 467).—It has been previously shown that dibasic organic acids can be partly extracted from aqueous solutions of their acid salts by treatment with ether, and McCoy has based a method of estimating the ratio of the first and second dissociation constants of such acids on this fact. The authors have repeated Chandler's work with camphoric and fumaric acids, and confirm his results. They have also applied the method to the determination of the second dissociation constant of homophthalic acid ($10^6k_1=191$), and obtained the value $k_1:k_2$ 212 (for $c=0.001$), and therefore the value $10^6k_2=0.9$. When contrasted with glutaric acid, which also contains the carboxyl groups in the 1:3-position ($10^6k_1=47.4$, $k_1:k_2=14$, $10^6k_2=3.38$), the ratio $k_1:k_2$ appears greatly increased, and here, as in other cases, to be subject to constitutive influences as well as to those due to the relative position of the carboxyl groups. Experiments with benzylmalonic acid and β -phenylglutaric acid show that the ratio of the constants, in comparison with those of the parent substances, is not greatly affected by the entry of a substituent in the symmetrical position. Comparison of δ -keto- β -phenyladipic acid,



($10^6k_1=9300$, $k_1:k_2=850$, $10^6k_2=11$), with adipic acid ($10^6k_1=37.6$, $k_1:k_2=15.7$, $10^6k_2=2.4$) shows a considerable increase in the first dissociation constant which can with certainty be ascribed to the presence of the carbonyl group; in addition, both the ratio $k_1:k_2$ and k_2 are increased, which is not in accordance with Smith's rule (*A.*, 1918, ii, 155) that a substituent has an unlike influence on the two carboxyl groups.

The statement of Thoms and Sabalitschka (*loc. cit.*) that phthalic

acid can be extracted by ether from aqueous solutions of its normal sodium salt could not be confirmed, nor do the authors find that phthalic acid suffers partial dehydration when its ethereal solution is evaporated on the water-bath.

H. W.

Chemical Processes in Solution and their Velocity.

MAX TRAUTZ (*Zeitsch. anorg. Chem.*, 1919, **106**, 149—188).—A purely mathematical paper in which the theory of gas reactions (compare A., 1918, ii, 151) is discussed in relation to the quantum theory and is applied to reactions in solution. Owing to the nature of the paper, satisfactory abstraction is impossible, but it may be stated that it is found that the integration constant of the reaction velocity in solution is identical with that in gases.

E. H. R.

The Law of Action of Sucrase: Influence of Viscosity on the Velocity of Hydrolysis.

H. COLIN and (MLLE.) A. CHAUDUN (*Compt. rend.*, 1919, **168**, 1274—1276. Compare A., 1918, i, 414; ii, 357).—The authors show that the velocity of hydrolysis of sucrose, the amount of sucrase remaining constant, is directly proportional to the fluidity of the solution. The ratio dV/dF , for solutions of varying sucrase-content, is proportional to the amount of sucrase present for a given sucrose concentration.

W. G.

The Hydrolysis of Ethyl Acetate.

L. BERCZELLER (*Oesterr. Chem. Zeit.*, 1919, **22**, 66—67).—The hydrolysis of ethyl acetate by hydriodic, hydrobromic, hydrochloric, and nitric acids has been studied with the object of determining the effect, if any, of the anion on the rate of the reaction. For each experiment, 10 c.c. of $N/2$ -ethyl acetate solution were mixed with 1, 2.5, 5, 10, or 40 c.c. of $N/2$ -acid solution and allowed to remain for times varying from a quarter of an hour to twenty-eight hours, at the end of which time the solution was titrated with $N/5$ -potassium hydroxide. The rates of hydrolysis are not equal for the different acids, the strengths of the acids being in the order $HI > HBr > HCl > HNO_3$. It is thus shown that in this typical case of catalysis the effect is not confined to the hydrogen ion, the chemical nature of the anion having the same influence here as in the so-called neutral salt action. The presence of iodine in the hydriodic acid was found to have a retarding influence on the reaction.

E. H. R.

Definition of the Terms: Explosion, Explosive Action, Thermite.

A. LANGHAUS (*Zeitsch. ges. Schiess. u. Sprengstoffw.*, 1918, **13**, 310—313; from *Chem. Zentr.*, 1919, i, 692—693. Compare this vol., ii, 219).—The definitions given in the literature lay stress on the function of gaseous factors in explosive decomposition and scarcely mention the importance of chemical decomposition, to which the author attributes prime importance, since actual explosions and explosive actions can be distinguished by it. The

following definitions only take into account the nature of the reaction; a definition in the strict physicochemical sense will be given later.

True explosion is the chemical decomposition of a substance in a definite manner which is distinguished by development of heat (chemical importance), sound (physical importance), and destruction of the immediate surroundings in consequence of high velocity of decomposition (technical importance). In decomposition of this kind, gases, either pre-formed or generated, are the chief agents. (1) *Direct Gas Explosions*.—The pre-formed gases are the actual carriers of the explosion, whilst the gaseous products cause the external physical and technical effects; the explosion may be total, as with oxyhydrogen gas, or partial, as with gas and solid or liquid substance, as in the cases of dust explosions, ether, and petroleum explosions. (2) *Indirect Gas Explosions*.—The gases do not react chemically and are not the carriers of the actual explosion, but merely cause the physical and technical effects. Two cases are to be distinguished, in the first of which a gas is present in which the solid or liquid substance explodes (silver acetylide, aluminium, or magnesium with an oxygen carrier, potassium chlorate and antimony sulphide, percussion gases), whilst in the second class the gas is generated by decomposition of solid or liquid substances (true explosives, such as nitroglycerol, gunpowder, picric acid). The substances capable of such decomposition are termed explosive substances.

Explosion-like actions are such as show external characteristics similar to those outlined above, but do not involve chemical action. With gaseous substances, gas may be pre-formed (lightning in air, explosion of bombs filled with compressed gas) or may be generated (boiler explosions, quicklime and water in a closed vessel); with liquids, such action is observed in the case of vessels filled with liquid, and examples with solids are afforded by Rupert's drops and explosive antimony. H. W.

Emission Spectra and Atomic Structure. JOHN WILLIAM NICHOLSON (T., 1919, 115, 855—864).—A lecture delivered before the Chemical Society on March 6th, 1919.

The Quantum Theory and New Theories of Atomic Structure. JAMES HOPWOOD JEANS (T., 1919, 115, 865—871).—A lecture delivered before the Chemical Society on May 1st, 1919.

Arrangement of Electrons in Atoms and Molecules. IRVING LANGMUIR (*J. Amer. Chem. Soc.*, 1919, 41, 868—934).—A theoretical paper in which a theory of the arrangement of electrons in atoms and molecules is put forward; this theory is essentially an extension of Lewis's theory of the cubical atom (A., 1916, ii, 310). The electrons in atoms are either stationary or rotate, revolve or oscillate, about definite positions in the atom.

In the most stable atoms, namely, those of the inert gases, the electrons have positions symmetrical with respect to a plane (equatorial plane) passing through the centre of the nucleus of the atom. No electrons lie in the equatorial plane. There is an axis of symmetry (polar axis) at right angles to this plane through which four secondary planes of symmetry pass, forming angles of 45° with each other. These atoms have the symmetry of a tetragonal crystal. The electrons of any atom are distributed through a series of concentric, nearly spherical shells, all of equal thickness. The mean radii of the shells are in the ratio 1:2:3:4, and the effective areas are in the ratio $1^2:2^2:3^2:4^2$. Each shell is divided into cellular spaces or cells occupying equal areas and symmetrically distributed over the surface of the shell. The first shell contains 2 cells, the second 8, the third 18, and the fourth 32. Each cell in the first shell can contain only one electron, but every other cell can contain either one or two electrons. The inner cells must have their full quota of electrons before the outside shell can contain any. No cell in the outside shell can contain two electrons until all other cells in this layer contain at least one. The electrons in the same cell neither repel nor attract one another, which implies a magnetic attraction that overcomes the electrostatic repulsion. When the number of electrons in the outside layer is small, the arrangement of the electrons is determined by the magnetic attraction of the underlying electrons, but when the number of electrons increases, especially when the layer is nearly complete, the electrostatic repulsion to the underlying electrons and of those in the outside shell becomes predominant. The properties of the atom are determined primarily by the number and arrangement of electrons in the outside shell and by the ease with which the atom is able to revert to more stable forms by giving up or taking up electrons. The stable and symmetrical arrangements of electrons corresponding with the inert gases are characterised by strong internal and weak external fields of force. The smaller the atomic number, the weaker the external field. The most stable arrangement of electrons is that of the pair in the helium atom. A stable pair may also be held by (a) a single hydrogen nucleus; (b) two hydrogen nuclei; (c) a hydrogen nucleus and the kernel of a second atom; (d) very rarely by two atomic kernels. The next most stable arrangement of electrons is the octet, that is, a group of eight electrons like that in the second shell of the neon atom. Any atom with atomic number less than 20, which has more than three electrons in its outside layer, tends to take up enough electrons to complete its octet. Two octets may hold one, two, or three pairs of electrons in common. One octet may share one, two, three, or four pairs of its electrons with one, two, three, or four other octets. One or more pairs of electrons in an octet may be shared by the corresponding number of hydrogen nuclei. No electron can be shared by more than two octets. This theory explains the periodic properties of all the elements, including those of the eighth group and the rare earths.

It accounts for the magnetic and physical properties as well as the chemical properties. It leads to a simple theory of valency for both polar and non-polar substances. It explains the structure of compounds, which, according to Werner's theory, are second-order compounds with a co-ordination number equal to four. According to the present theory, such compounds are to be regarded as typical primary valency compounds. This valency theory is based on the equation $e = 8n - 2p$, where e is the total number of available electrons in the shells of all the atoms in a molecule, n the number of octets forming the outside shells, and p the number of pairs of electrons held in common by the octets. The theory leads to definite conceptions of the positions of the electrons in the molecules or space lattices of compounds. The structures of the molecules of nitrogen, carbon monoxide, hydrogen cyanide, and nitric oxide are exceptional, because the kernels of both atoms are contained within a single octet. This accounts for the practically identical physical properties of nitrogen and carbon monoxide and for the abnormal inertness of nitrogen. J. F. S.

The Derivation of the Periodic System of the Chemical Elements from the Electron Theory. HEINRICH TEUDT

(*Zeitsch. anorg. Chem.*, 1919, 106, 189—208).—Starting with the conception of the atom as a positively charged nucleus surrounded by rotating negative electrons, the author shows how many of the important properties of the periodic system of the elements follow from this conception. Two kinds of electrons are distinguished, an inner sphere firmly held by the attractive force of the positive nucleus and an outer sphere of valence electrons, through which combination with other atoms takes place. The rotating electrons are probably distributed symmetrically on spherical surfaces as near the equatorial zone of the atom as possible. Hydrogen is the only element which has only valence electrons, since its one electron functions in this manner. The two electrons of helium are both bound in the inner sphere, the element having no valence electrons, and the same is true of the other inert gases. The remaining elements have electrons of both kinds. Those of the first horizontal series have two electrons in the inner sphere, whilst the number of possible valence electrons increases from lithium (1) to fluorine (7). Some of the valence electrons tend to be retained in the inner sphere, however, for instance, when carbon becomes bivalent, nitrogen trivalent, oxygen bivalent, and fluorine univalent. In the second horizontal series, the inner sphere contains at least ten electrons, in the third series eighteen, and so on.

The metals are distinguished from the metalloids by their more mobile or less firmly held valence electrons. Passing from left to right in a horizontal series, the number of positive charges on the nucleus steadily increases, whilst the number of inner electrons remains constant, and in order to retain their position the latter must increase their centrifugal force by increasing their rotation velocity. At the same time, the valence electrons must increase

their rotation velocity to a corresponding degree to prevent disruption of the atom, and the whole electron system becomes more stable. It follows that the metalloid character of the elements increases from left to right of a horizontal series. In the third, fifth, and seventh horizontal series, however, the metallic character is maintained throughout. To explain this irregularity, it is supposed that in these series the inner sphere is made up of an odd number of rings of electrons, the central ring occupying the equatorial position. This central ring of electrons intercepts lines of force which, in the case of the second, fourth, and sixth series with even numbers of rings of electrons in the inner sphere, would serve to hold the valence electrons with greater force. It follows that the outer electrons of odd series are more mobile than those of the even series, and the elements of the former are therefore more metallic. The appearance of the iron, ruthenium, and osmium triads is attributed to the relative instability of the electron systems developed at the end of the third, fifth, and seventh horizontal series. The elements copper, silver, and gold are closely related to the respective triads which they follow, and should not be placed in Group I. As the number of electrons in the atom increases, the forces retaining the valence electrons become weaker, and consequently the metallic character of the elements becomes more marked with increasing atomic weight. The periodic progression of the atomic volumes of the elements is discussed in terms of the electron theory. E. H. R.

A New Periodic Classification of the Chemical Elements.

MARC CHAUVIERRE (*Bull. Soc. chim.*, 1919, [iv], **25**, 297—305).—Marking off the atomic weights as abscissæ and the principal valencies of the elements (from zero to four) as ordinates, a periodic curve the period of which is double is obtained, the elements of the iron, palladium, didymium, and platinum families, the atomic weights of which are close together, being placed above the level of quadrivalency. The elements which occur in the same periodic position on the curve have generally similar chemical properties and correspond with the natural groups of elements. The elements may also be arranged by this method in a table similar to that of Mendeleev. W. G.

Annual Report of the International Committee on Atomic Weights (T., 1919, 115, 879—885).

The Alchemists Known as Hollandus. EDMUND O. VON LIPPMANN (*Chem. Zeit.*, 1919, **43**, 265—267, 286—288, 301—303).—In a long contribution to the discussion on the authenticity and period of Jan Isaac and Isaac of Holland, the author maintains his original view (*A.*, 1916, ii, 525) against the criticism of Schelenz (*A.*, 1917, ii, 529). E. H. R.

Basil Valentine. B. NEUMANN (*Zeitsch. angew. Chem.*, 1919, 32, I, 184).—Polemical. A reply to Hommel (this vol., ii, 224).
S. S. A.

Trustworthiness of the Balance over Long Periods of Time. GEORGE DEAN (*T.*, 1919, 115, 826—828).

Laboratory Condensers for Use in Reflux Condensation and Distillation Apparatus. O. FAUST (*Zeitsch. angew. Chem.*, 1919, 32, I, 183—184).—A description is given of condensers, especially suitable for use as reflux condensers, which are provided at the same end with inlet and outlet tubes, one of which passes inside the jacket to the other end of the condenser, whereby counter-current cooling is obtained. The jacket is provided with an air outlet tap. Of the various designs illustrated, one is suitable for connexion in the usual way, another for suspension in the neck of the flask without cork connexion, and a third for fitting bodily into the neck of the distillation vessel.
S. S. A.

Simple Efficient Vacuum Pump for Laboratory Use. ALFRED MAGNUS (*Ber.*, 1919, 52, [B], 1194).—A claim for scientific priority against Volmer (this vol., ii, 225). The application of a current of mercury vapour to the production of high vacua has been utilised by the author (*Inaug. Diss.*, München, 1905).
H. W.

Lecture Experiments [to Illustrate] the Reduction of Hydrogen-ion Concentration. L. GRÜNHUT (*Zeitsch. Elektrochem.*, 1919, 25, 184—185).—Two experiments are described by which the reduction of the hydrogen-ion concentration may be demonstrated.

(1) By removal of hydrogen ions: 10 c.c. of 0.1*N*-hydrochloric acid are placed in each of two 100 c.c. cylinders, and a few drops of a solution of dimethylaminoazobenzene solution added. One cylinder is filled to the mark with distilled water and the other with a 0.1*N*-solution of disodium hydrogen citrate. The water solution is red in colour, whilst the other solution becomes yellow. The aqueous solution contains 9.7 mg.-ion per litre ($P_{\text{H}^+} = 2.013$), whilst the citrate solution contains 0.015 mg.-ion per litre ($P_{\text{H}^+} = 4.83$), that is, the hydrogen-ion concentration has been reduced to 1/650 of its original value. The colour change of dimethylaminoazobenzene occurs between $P_{\text{H}^+} = 3$ and $P_{\text{H}^+} = 4$.

(2) By repressing the ionisation: 100 c.c. of tartaric acid (40 grams per litre) are placed in each of two 100 c.c. cylinders and coloured blue by the addition of a few drops of methyl-violet solution. To one cylinder, 4 grams of finely powdered sodium tartrate are added; this, when dissolved, will change the colour to violet. The water solution contains 17.00 mg. H^+ ion per litre ($P_{\text{H}^+} = 1.77$), whilst the tartrate solution contains 0.96 mg. H^+ ion per litre ($P_{\text{H}^+} = 3.02$). The neutral point of methyl-violet lies between $P_{\text{H}^+} = 2$ and $P_{\text{H}^+} = 3$.
J. F. S.

Inorganic Chemistry.

Physico-chemical Revision of the Atomic Weight of Bromine: Necessity of Correcting the Atomic Weight of Silver. PH. A. GUYE (*J. Chim. Phys.*, 1919, **17**, 171—186).—From the experiments of Moles (A., 1916, ii, 42, 526) and Reiman (A., 1917, ii, 137, 200), the weight of the normal litre of hydrogen bromide has been calculated to the value 3.64423 grams. The weight of a litre of hydrogen bromide at 0° and under a pressure of 2/3 or 1/3 atm. is given by 2.42197 grams and 1.20729 grams respectively. The divergences from Avogadro's law $(1+\lambda)$ and from the compressibility (A'_0) have been found to be $(1+\lambda)=1.00934$ and $A'_0=0.00925$ (see this vol., ii, 318). From these values, the atomic weight of bromine is calculated to 79.920. This value is slightly greater than the value obtained from the ratio Ag:Br, consequently it is suggested that the atomic weight of silver ought to be reduced to 107.87. J. F. S.

Recovery of Iodine from its Residues. F. ARNDT (*Ber.*, 1919, **52**, [B], 1131—1134).—The residues are placed in a large flask provided with a rubber stopper which carries a tube reaching nearly to the bottom of the liquid. The other end of the tube is connected with a reversed wash-bottle and a source of oxygen. The residues (which should not more than half fill the flask) are acidified with crude sulphuric acid, and oxygen is passed into the flask. A small quantity of nitrite solution is added, the flask is securely corked, and passage of the oxygen is continued into the well-shaken liquid. Completion of the action is indicated by cessation of the oxygen absorption, when a further small quantity of nitrite should be added to make certain that all the iodine has separated. The crude iodine is purified by distillation with steam, the vapours being passed directly into a large Erlenmeyer flask, which is cooled by water and is also provided with a long, upright tube to serve as air condenser. The iodine which is thus obtained retains water with considerable obstinacy, and is most easily dried by warming it on the water-bath in a porcelain dish covered by a clock-glass; the latter is frequently removed and the deposit of moisture and iodine is scraped off. As soon as the sublimate appears perfectly dry, the main portion may safely be regarded as dry also. The iodine so obtained is pure.

If the original solution is free from organic matter of high molecular weight, such as starch, the distillation with steam may be omitted. H. W.

Electrolytic Production of Fluorine. W. L. ARGO, F. C. MATHERS, B. HUMISTON, and C. O. ANDERSON (*J. Physical Chem.*, 1919, **23**, 348—355).—The authors have prepared fluorine by the

electrolysis of molten potassium hydrogen fluoride. The electrolysis is effected in an electrically heated copper vessel which serves as cathode; the anode is made of graphite. The anode is enclosed in a permeable diaphragm, which prevents the hydrogen liberated at the cathode mixing with the fluorine. As the electrolysis proceeds, potassium fluoride and copper fluoride are deposited from the fusion, and after a while it becomes necessary to regenerate the electrolyte. The most efficient conditions for work are a temperature of 240—250° and a current of 10 amperes at 15 volts. Using these conditions, the current efficiency is about 70%. In the preparation, the potassium acid fluoride must be absolutely dry, and since this is difficult to obtain and keep on account of the hygroscopic properties of the salt, the authors prefer the corresponding sodium salt, which has the advantages: (i) it is non-deliquescent, (ii) it decomposes below the fusion temperature, (iii) it contains a larger quantity of available hydrofluoric acid, and (iv) it is considerably less expensive. The properties of fluorine which may be used for its detection are: (i) its not unpleasant odour (fluorine in small quantities is non-toxic, but long exposure to larger quantities produces headache); (ii) the unlighted gas issuing from a Bunsen burner is immediately ignited by fluorine; (iii) sulphur and soft charcoal are quickly ignited when the gas comes into contact with them.

J. F. S.

Constitution of Sulphur Vapour. JAMES J. DOBBIE and J. J. FOX (*Proc. Roy. Soc.*, 1919, [A], **95**, 484—492).—The absorption spectrum of sulphur vapour has been photographed at the temperatures 380—1080°. Sulphur vapour was produced in a silica tube 100 mm. long and 12 mm. diam., and the measurements were made with a large Hilger spectrograph. Illumination was produced by a Nernst lamp for the visible region and the ultra-violet down to λ 3100, and for the region beyond the range of the Nernst lamp a cadmium arc was employed. Weighed quantities of sulphur were vaporised in the tube, which had previously been sealed at a pressure of 8 mm., the gaseous content being nitrogen; a further series of experiments was made at atmospheric pressure. The spectrum shortens as the temperature is raised to 650°, after which it lengthens again. The maximum absorption therefore occurs at this point. The authors find on extrapolating the vapour density results of Biltz (A., 1888, 1027) that at the temperature 650° the density corresponds with a molecule S_3 . The authors are therefore of the opinion that at suitable temperatures sulphur vapour contains the molecules S_2 , S_3 , and S_8 .

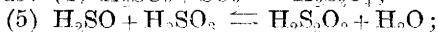
J. F. S.

The Reduction of Sulphurous Acid by Hydrogen Sulphide in Aqueous Solution. ERNST HEINZE (*J. pr. Chem.*, 1919, [ii], **99**, 109—178).—For the quantitative investigation of the reaction between sulphur dioxide and hydrogen sulphide in aqueous solution at different temperatures, an apparatus was constructed by means of which accurately measured quantities of the

gases could be brought successively into the reaction flask, in which water was already present, with complete exclusion of air. The course of the reaction was found to be very complicated and to involve a number of reversible reactions. It depends both on the relative proportions of the reacting gases used and on the order of addition. A considerable part of the paper is devoted to a description of the special methods devised for the analysis of the reaction liquor. It was found that the sulphur formed in the reaction could be obtained in a readily filterable form if a small quantity of lanthanum chloride was present in the solution. Any remaining hydrogen sulphide was estimated by precipitation with cadmium sulphate; sulphur dioxide was removed by a current of nitrogen, collected in sodium hydroxide solution, and estimated iodometrically, whilst polythionic acids were determined by titrating the remaining solution with barium hydroxide.

It is established, first, that sulphur dioxide enters into the reaction in the form of sulphurous acid, not in the anhydride form. The primary reaction appears to be represented by the reversible equation $\text{H}_2\text{SO}_3 + \text{H}_2\text{S} \rightleftharpoons \text{H}_2\text{SO}_2 + \text{H}_2\text{SO}$. Precipitation of sulphur is caused by the decomposition of the compound H_2SO_2 , which is assumed to be of the hydrogen peroxide type. This compound is also supposed to be formed by the further action of hydrogen sulphide on the sulphonylic acid, thus: $\text{H}_2\text{SO}_2 + \text{H}_2\text{S} \rightleftharpoons 2\text{H}_2\text{SO}$. Consequently, the final result of the interaction of one mol. of sulphurous acid with two mols. of hydrogen sulphide is given by the equation $2\text{H}_2\text{S} + \text{SO}_2 = 3\text{S} + 2\text{H}_2\text{O}$. The reaction only comes to completion, however, after several months. The final state is reached more quickly in presence of excess of hydrogen sulphide. It is shown experimentally that hydrogen sulphide also reacts with polythionic acids to form sulphur and water.

When excess of sulphurous acid is present, less sulphur is precipitated and more polythionic acid formed. After about a day, a condition of equilibrium obtains. If, now, the precipitated sulphur is filtered off and the excess of sulphur dioxide removed by a current of nitrogen, in a short time more sulphur comes down and sulphur dioxide again appears in the solution. It is shown that the sulphur, when once precipitated, takes no further part in the process, and the reversible reactions are supposed to involve the polythionic acids, sulphurous acid, and the compounds H_2SO_2 and H_2SO , thus: (4) $\text{H}_2\text{SO}_3 + \text{SO}_2 \rightleftharpoons \text{H}_2\text{S}_2\text{O}_4$;



(6) $\text{H}_2\text{S}_2\text{O}_4 + \text{H}_2\text{S}_2\text{O}_3 \rightleftharpoons \text{H}_2\text{S}_4\text{O}_6 + \text{H}_2\text{O}$; (7) $\text{H}_2\text{S}_4\text{O}_6 + \text{H}_2\text{S}_2\text{O}_3 \rightleftharpoons \text{H}_2\text{S}_6\text{O}_{11} + \text{H}_2\text{SO}_3$. With increasing concentration of sulphur dioxide, the proportion of tetrathionic acid increases, whilst that of pentathionic acid decreases. This is attributed to the dehydration of the sulphurous acid owing to the increasing acidity of the solution, with consequent increase in the production of $\text{H}_2\text{S}_2\text{O}_4$ by equation (4).

When solutions containing excess of sulphur dioxide are allowed to remain for several weeks, increasing quantities of sulphuric acid

are formed, but the mechanism of this change cannot at present be explained. Possibly it is due to the decomposition of trithionic acid, which may be formed in small quantities and is known to decompose into sulphuric acid, sulphur dioxide, and free sulphur.

E. H. R.

Action of Sodium Thiosulphate on the Hypochlorites.

F. DIÉNERT and F. WANDENBULCKE (*Compt. rend.*, 1919, **169**, 29—30).—A quantitative study of the interaction of sodium thiosulphate and sodium hypochlorite in dilute solutions shows that the reaction proceeds according to the equation $3\text{Na}_2\text{S}_2\text{O}_3 + 5\text{Cl}_2 + 5\text{H}_2\text{O} = \text{Na}_2\text{SO}_4 + 8\text{HCl} + \text{H}_2\text{SO}_4 + \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaCl}$ or $5\text{NaOCl} + 3\text{Na}_2\text{S}_2\text{O}_3 + 5\text{H}_2\text{O} = 2\text{Na}_2\text{SO}_4 + \text{Na}_2\text{S}_4\text{O}_6 + 5\text{NaCl} + 5\text{H}_2\text{O}$. In the presence of acids, however, or even in the presence of sodium hydrogen carbonate, much less sodium thiosulphate is required, the reaction being $\text{Na}_2\text{S}_2\text{O}_3 + 4\text{Cl}_2 + 5\text{H}_2\text{O} = 2\text{NaHSO}_4 + 8\text{HCl}$.

W. G.

Selenic Acid and Copper Selenate. L. M. DENNIS and J. P. KOLLER (*J. Amer. Chem. Soc.*, 1919, **41**, 949—970).—Selenium has been obtained from smelter flue-dust by fusing a mixture of 300 grams of flue-dust, 200 grams of anhydrous sodium carbonate, and 775 grams of sodium peroxide in a large nickel crucible until the mass melted quietly. After cooling, the product was treated with water and insoluble material filtered off; it was then nearly neutralised with hydrochloric acid, which precipitated most of the zinc and aluminium. After filtration, a large volume of hydrochloric acid was added, and the solution boiled for thirty minutes to reduce selenic acid to selenious acid; any silica present was precipitated at this stage; the filtrate was then heated to 80° and treated with sodium sulphite in small quantities. The selenium separates, and is converted into the grey modification by digesting it with the solution for several hours at 80°.

Anode slimes containing 96% of selenium were also used to prepare the pure element. The slime was added to concentrated nitric acid to which one-fifth of its volume of water had been added; a vigorous action ensued, and when this had moderated, the mixture was heated to complete the oxidation. The solution was filtered, and a viscous, dark green liquid obtained which was evaporated to dryness. The residue was taken up with hydrochloric acid (3:1) and the selenium precipitated by sulphur dioxide or sodium sulphite.

Pure selenium dioxide is prepared from selenium by dissolving the substance obtained above in nitric acid and evaporating the solution to dryness. The crude dioxide thus obtained was placed in one end of a glass tube 85 cm. long and 3.5 cm. diameter. The tube was covered with asbestos paper and placed in a 60 cm. combustion furnace; a 2 cm. thick plug of glass wool was placed in the middle of the tube. The tube was so arranged in the furnace that

only a small length protruded at the cold end. On heating the crude dioxide, it sublimed and condensed on the protruding part of the tube, and as this became full, more of the tube was pushed out of the furnace.

Selenious acid was prepared directly from anode slimes by oxidising with nitric acid and evaporating until a syrupy solution was obtained. On cooling, large crystals separated, and after four recrystallisations from water, pure selenious acid, quite free from tellurium, was obtained.

Tellurium may be detected in the presence of selenium by dissolving 10—20 grams of the oxide in hydrochloric acid (D 1.16), heating to 90°, and saturating with sulphur dioxide. The precipitated selenium is filtered off and the filtrate diluted with an equal volume of water and saturated cold with sulphur dioxide. An immediate black precipitate of tellurium is formed if this element is present. A yield of 1200 grams of selenious acid was obtained from 3000 grams of slimes.

Pure selenic acid has been prepared (i) by the oxidation of silver selenite by means of bromine, (ii) by the oxidation of copper selenite by chlorine, and (iii) by the electrolytic oxidation of selenious acid. In the last-named method, the most efficient yield is obtained when lead dioxide anodes, in thimbles, are used.

Selenious acid may be detected in the presence of selenic acid on the basis of the reaction $\text{H}_2\text{SeO}_3 + 4\text{HI} = \text{Se} + 4\text{I} + 3\text{H}_2\text{O}$. Concentrated selenic acid will also oxidise hydriodic acid, but if the solution is dilute, selenic acid will remain unchanged. If, therefore, small quantities of potassium iodide are added to solutions containing both selenious and selenic acid in test-tubes 15 cm. long, there will be a yellow colour produced, due to iodine being liberated, and when the colour of the iodine is discharged by the addition of a drop or two of sodium sulphite, the red turbidity due to free selenium is visible. If the selenic acid is more concentrated than 0.8%, iodine may be liberated by it, but as the hydriodic acid is not concentrated, the reaction goes no further. This reaction is capable of detecting 1 part of selenium dioxide in 18,400 parts of selenic acid, or 1 part of selenium dioxide in 2,500,000 parts of solution.

Sulphuric acid in the presence of selenic acid may be detected in the following manner. Selenic acid is diluted to 4%, placed in a 350 c.c. beaker, 10 c.c. of 90% hydrazine hydrate added, and heated to 60°. Sufficient concentrated hydrochloric acid (5 c.c.) is added to make the liquid distinctly acid, and the mixture boiled for an hour. After cooling, the precipitated selenium is filtered off, and the process repeated until no more selenium is deposited. The filtrate is then evaporated to 25 c.c., and 2 c.c. of 10% barium chloride solution are added, and the mixture kept at 80° for an hour, when a white turbidity is produced if sulphuric acid is present. This reaction is visible if 1 mg. of barium sulphate is formed, and it is possible to detect 1 part of sulphuric acid in the presence of 10,000 parts of selenic acid.

All attempts to prepare perselenic acid and perselenates by electrolysis gave negative results.

The monohydrate of copper selenate is produced from the pentahydrate by heating the latter at 102° for two hours. The pentahydrate is completely dehydrated at 230 — 235° , and the anhydrous selenate is stable up to 280° . The pentahydrate used in these experiments was prepared by the action of chlorine on copper selenite, and contained copper chloride; this was removed by extracting with acetone in a Soxhlet extractor. In this process, the pentahydrate lost $2\text{H}_2\text{O}$ and the trihydrate was formed; this substance has a pale blue colour.

Ammonia derivatives of copper selenate have been prepared by methods analogous to those used by Horn and Taylor (A., 1904, ii, 662) in the preparation of the corresponding derivatives of copper sulphate. (i) *Copper selenate tetra-ammoniate monohydrate*, $\text{CuSeO}_4 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$, is prepared by digesting 100 grams of copper selenate pentahydrate with 125 c.c. of ammonium hydroxide (0.96) until it has dissolved; ammonia gas is then led in, and in a short time clusters of deep bluish-violet crystals separate. The crystals were dried by suction and finally air-dried. It is quite stable when kept over lime, but loses ammonia in the air; it crystallises in slender, orthorhombic prisms. (ii) *Copper selenate triammoniate monohydrate*, $\text{CuSeO}_4 \cdot 3\text{NH}_3 \cdot \text{H}_2\text{O}$, is prepared by exposing the last described compound to a current of air for about twenty-four hours. It is a blue compound which dissolves in water to give a blue solution; this on dilution becomes lighter in colour and deposits a basic salt. (iii) *Copper selenate tetra-ammoniate*, $\text{CuSeO}_4 \cdot 4\text{NH}_3$, is prepared from the first-named compound by placing it moist in a desiccator over lime at 25 mm. pressure and keeping it there for seven days. It is of a lighter bluish-violet colour than the hydrated salt; it gives off ammonia when exposed to the air, but is stable in a vacuum over lime.

J. F. S.

Formation of Ammonia by Means of an Electric Arc : Influence of Diminishing the Pressure. E. BRINER and A. BAERFUSS (*J. Chim. Phys.*, 1919, 17, 71—140. Compare this vol., ii, 148).—The synthesis of ammonia from a mixture of nitrogen and hydrogen at reduced pressures by means of an alternating arc between electrodes of various metals has been studied under a long series of widely varying experimental conditions. It is shown that at sufficiently low pressures (150 mm. and below) the arc assumes the appearance of a luminous sheath, which surrounds the electrodes and becomes longer the lower the pressure and the larger the current. This sheath plays an important part in the synthesis of ammonia. On reducing the pressure, it is noted that successive decreases in the voltage of the arc have nearly the same effect in the two pure gases and their mixtures. At pressures of the order 600—700 mm., an increase in the arc current leads to an increase in the energy yield (Rdt), which is due to a lowering of the

voltage. Working at pressures of the order 100 mm. with the theoretical mixture of gases, there is an improvement in the value of Rdt which is to be attributed, for the most part, to the lowering of the voltage. At this pressure and with platinum electrodes, an increase in the nitrogen percentage leads to an increased quantity yield (Q) of about 200% for the optimum mixture of five volumes of nitrogen to one volume of hydrogen. Using different metals as electrodes, it is found that the metals of the platinum group give the best results, platinum itself being most efficient; these metals are followed in efficiency by tungsten and copper. Iron and nickel are very much less effective than the other metals mentioned, and for these the optimum yield is obtained from the theoretical mixture at all pressures. The presence of moisture does not appear to affect the synthesis; the presence of oxygen in small quantities in certain circumstances acts favourably on the reaction. At reduced pressures, the influence of the arc current appears to be connected with the temperature produced at the electrodes; for every electrode there is an optimum diameter for every current. For currents up to 0.020 amp., cooling of the region containing the arc does not increase the yield. At low pressures, the yields are almost independent of the distance between the electrodes, consequently it is advisable to reduce this space as much as possible, since it only plays a secondary part in the reaction. There is no appreciable formation of ammonia when nitrogen and hydrogen, which have been submitted to the arc, are allowed to mix. The foregoing results confirm in the main the theory of the formation of ammonia put forward by the authors. This theory states that ammonia is formed by the action of a high temperature followed by a kinetic phenomenon in the colder regions where the ammonia is stable in the concentration produced, rather than by the establishment of an equilibrium in the very cold regions. In the relatively cold regions, which are near the luminous sheath, the formation occurs between the elements which have previously been rendered active by contact with the electrodes. The activation of the elements appears to consist of the dissociation of the molecules into atoms at the very high temperature of the arc, and is favoured by a diminution of the pressure. Active nitrogen, described by Strutt, does not appear to take any part in the synthesis, and at the pressures employed does not appear to be formed. J. F. S.

Relations between Nitrogen Peroxide and Nitric Acid.

P. PASCAL and GARNIER (*Bull. Soc. chim.*, 1919, [iv], **25**, 309—321). —Results obtained for the density of nitrogen peroxide over the temperature range 0—21.5° are in agreement with those of Cundall (compare T., 1891, **59**, 1076), being represented by the equation $D'_1 = 1.490 - 0.00215t$. The density of nitrogen peroxide is lowered by the addition of nitrous anhydride, the variations of density with the composition of the mixture obeying a linear law.

The density of nitric acid shows a marked increase with the addition of nitrogen peroxide (compare Lunge and Marchlewsky,

Zeitsch. angew. Chem., 1912, 10), reaching a maximum when the mixture contains about 42·5% by weight of the peroxide. This corresponds with a hydrate, $N_2O_5 \cdot N_2O_4 \cdot H_2O$, and the existence of this is confirmed by a thermal study of the reciprocal solubilities of nitric acid and nitrogen peroxide. This hydrate is stable below $-48\cdot5^\circ$, and at this temperature dissociates, liberating nitrogen peroxide.

Sulphuric acid is not appreciably soluble in nitrogen peroxide, but when added to anhydrous nitric acid or the acid containing a little water, it does not appreciably alter the solubility of the peroxide in the acid providing the mixture does not contain more than 30% of sulphuric acid, the water content being the principal factor of solubility.

W. G.

Some Properties of Acid Phosphates. A. JOANNIS (*Compt. rend.*, 1919, 168, 1202—1203).—Neither disodium hydrogen phosphate nor potassium dihydrogen phosphate absorbs gaseous or liquid ammonia, and ammonium dihydrogen phosphate only absorbs it very slowly. Similarly, in the absence of water, magnesium ammonium phosphate cannot be obtained from magnesium hydrogen phosphate.

W. G.

Allotropy of Carbon. MAURICE COPISAROW (*Chem. News*, 1919, 118, 301—304).—The polyatomicity of the carbon molecule is proved by (i) the existence of several forms of carbon which are chemically and physically distinct from one another, (ii) the high volatilisation point, (iii) the general theory of the solid state, (iv) the products of moist oxidation, (v) the combustion of carbon, and (vi) the X-ray spectrometric study of the modifications of carbon. In accordance with the theory of allotropy (this vol., ii, 279), carbon may exist in three forms: (a) a non-rigid, molecular configuration, some valencies of which are free, (b) a rigid, molecular configuration, some valencies of which are free, and (c) a rigid, molecular configuration, all valencies of which are fixed. From a consideration of the heats of combustion, products of oxidation, and the physical properties of the three forms of carbon, it is shown that amorphous carbon is represented by *a*, graphite by *b*, and diamond by *c*. Possible configurations in keeping with the above are drawn in the paper.

J. F. S.

The Oxidation of Coal. FREDERICK VINCENT TIDESWELL and RICHARD VERNON WHEELER (*T.*, 1919, 115, 895—902).

The Preparation of Carbonyl Chloride by Means of Carbon Tetrachloride and Oleum or Ordinary Sulphuric Acid. V. GRIGNARD and ED. URBAIN (*Compt. rend.*, 1919, 169, 17—20).—With sulphur trioxide, carbon tetrachloride reacts according to the equation $2SO_3 + CCl_4 = COCl_2 + S_2O_5Cl_2$, but with pyrosulphuric acid the reaction is $SO_3 + H_2SO_4 + CCl_4 = COCl_2 + 2SO_3HCl$. With ordinary sulphuric acid in the presence of

infusorial earth as a catalyst, the reaction is $2\text{H}_2\text{SO}_4 + 3\text{CCl}_4 = 3\text{COCl}_2 + 4\text{HCl} + \text{S}_2\text{O}_5\text{Cl}_2$, together with a slight secondary reaction, $\text{S}_2\text{O}_5\text{Cl}_2 + \text{CCl}_4 = \text{COCl}_2 + 2\text{SO}_2\text{Cl}_2$. The principal objection to this second method is the presence of hydrogen chloride with the carbonyl chloride, but this may be got over to some extent by dissolving the carbonyl chloride in carbon tetrachloride, the hydrogen chloride being only slightly soluble in this solvent. [See, further, *J. Soc. Chem. Ind.*, 1919, August.] W. G.

Action of Concentrated Sulphuric Acid on Carbon Tetrachloride. CH. MAUGUIN and L. J. SIMON (*Compt. rend.*, 1919, **169**, 34—36. Compare Grignard and Urbain, preceding abstract).—Real sulphuric acid reacts with carbon tetrachloride at about 150° according to the equation $\text{CCl}_4 + \text{H}_2\text{SO}_4 = \text{SO}_3\text{HCl} + \text{COCl}_2 + \text{HCl}$. If an acid which is slightly aqueous is used, the water present is decomposed by the chlorosulphonic acid first formed, giving sulphuric acid and hydrogen chloride. Finally, the chlorosulphonic acid itself reacts with carbon tetrachloride, thus: $\text{CCl}_4 + 2\text{SO}_3\text{HCl} = \text{S}_2\text{O}_5\text{Cl}_2 + 2\text{HCl} + \text{COCl}_2$. The carbonyl chloride is purified by solution in carbon tetrachloride and subsequent distillation. W. G.

The Sulphones formed by the Iodides of Sodium, Rubidium, and Cæsium. R. DE FORCRAND and F. TABOURY (*Compt. rend.*, 1919, **168**, 1253—1257).—By the action of liquid sulphur dioxide on the iodides of sodium, rubidium, and cæsium, the authors have obtained sulphones of the type MI_3SO_2 , that of sodium being amorphous and the other two being soluble in excess of liquid sulphur dioxide, and crystallising from it on evaporation at 0° . W. G.

Stability of Sodium Thiosulphate Solutions. I. M. KOLTHOFF (*Pharm. Weekblad*, 1919, **56**, 878—888).—In general, the decomposition of thiosulphate solutions proceeds more rapidly in the light than in the dark. The oxidising action of the air may be prevented to some extent by covering the solution with a layer of light petroleum. The presence of alkaline substances prevents the decomposition almost completely. The addition of about 0.2 gram of sodium carbonate per litre is sufficient to ensure in great measure the stability of the solution. The accelerative effect of deposited sulphur on the decomposition is probably due to bacterial action. The decomposition may be retarded by the addition of 0.01 gram of mercuric iodide per litre of solution. W. S. M.

Sodium Hydrogen Sulphite Crystals ($\text{NaHSO}_3 \cdot 3\text{H}_2\text{O}$).—WALTHER SCHÜLER and ARNO WILHELM (*Zeitsch. angew. Chem.*, 1919, **.32**, 198—199).—The sodium hydrogen sulphite crystals deposited at low winter temperatures from aqueous solutions contain three molecules of water. They are 2—6 cm. long, 2—3 mm.

thick, hexagonal in section, and belong apparently to the rhombic system. At higher temperatures or when removed from the mother liquor, they rapidly lose water and disintegrate, leaving a residue of anhydrous sodium hydrogen sulphite containing sulphate and traces of pyrosulphite if they have been exposed to the air.

G. F. M.

Lime Mortars : Solution and Conversion of Solid Substances into Colloids. V. KOHLSCHÜTTER and G. WALTHER (*Zeitsch. Elektrochem.*, 1919, **25**, 159—183).—The rate at which calcium oxide, prepared from calcium carbonate, calcium hydroxide, and calcium oxalate, respectively, combines with water vapour at the ordinary temperature has been determined. The volume changes and the amount of water taken up have also been determined. The rate of absorption is shown to differ with the various samples of calcium oxide. Further, the rate of sedimentation of calcium hydroxide has been measured for calcium hydroxide prepared by slaking lime in water or solutions of calcium chloride, calcium nitrate, sodium chloride, potassium chloride, potassium nitrate, sodium hydroxide, sodium acetate, potassium thiocyanate, ammonia, ammonium oxalate, and sodium carbonate of various concentrations. The rate at which sedimentation occurs varies with the different electrolytes; some when in small concentrations increase the sedimentation velocity, and in large concentrations decrease it, whilst in other cases the reverse is the case. The velocity of sedimentation is greater when water is added to quicklime than when lime is added to water. Further, a difference is observed in the rate of sedimentation of calcium hydroxide produced by slaking lime in lime-water. The sedimented product of a suspension of calcium hydroxide in water is not the same as the product obtained by slaking lime in water and allowing it to settle. The results obtained indicate that in the production of a true solution of calcium hydroxide in water from lime, an intermediate colloidal state is first formed.

J. F. S.

Lead-Sodium-Mercury and Lead-Sodium-Tin Alloys. J. GOEBEL (*Zeitsch. anorg. Chem.*, 1919, **106**, 209—228).—A thermal investigation has been made of lead-sodium-mercury alloys containing up to 4% of sodium and 7% of mercury, and of lead-sodium-tin alloys containing up to 4% of sodium and 6% of tin. The lead-sodium binary alloys show a eutectic point at 308° with 2.7% of sodium, the eutectic consisting of mixed crystals of sodium and lead with a compound, probably Na_2Pb_5 , which corresponds with 4% of sodium. To obtain the equilibrium diagram of the lead-sodium-mercury alloys, sixty-three fusions were made. In presence of mercury up to 2%, the lead-sodium eutectic persists, but the eutectic point is lowered about 5°. With more mercury, up to 7%, the eutectic point disappears, but is still represented in the diagram by a minimum in the same position. Sodium is more soluble in the lead-mercury mixed crystals than in pure lead. A

plan of the space diagram with isothermal lines is given. The series of fusions with 3% of mercury was extended up to 12% of sodium. The liquidus line rises from 2.7% to about 5% of sodium, then falls to a eutectic point between 7 and 8% of sodium at 290°, and again rises to a high maximum at 354° with 10% of sodium. It then falls rapidly towards another eutectic line at 280°. The existence of at least two compounds is indicated, but their nature is not apparent.

To obtain the equilibrium diagram for the lead-sodium-tin system up to 4% of sodium and 6% of tin, forty-eight fusions were made. The space diagram consists of two surfaces meeting in a depression running parallel to the lead-tin side of the diagram. This depression represents the separation of a eutectic consisting of lead-sodium mixed crystals with an unknown compound. The temperature of the eutectic point falls with increasing quantities of tin from 308° to 296°. The lead-tin mixed crystals appear to dissolve no more sodium than pure lead.

E. H. R.

Reduction of Metallic Sulphides by Means of Aluminium.

N. PARRAVANO and P. AGOSTINI (*Gazzetta*, 1919, **49**, i, 103—115. Compare Parravano and De Cesaris, A., 1917, ii, 292).—The displacement of the metal of a sulphide by another metal in accordance with the equation $M^1 + MS \rightleftharpoons M^1S + M$ is considered in the two cases: (1) when the reacting compounds are able to exist together without mixing, and (2) when such compounds are more or less miscible in the liquid state alone or in both the liquid and solid states.

In the experiments made, the metallic sulphide was added to molten aluminium contained in a clay crucible, the reacting substances being taken in weighed quantities. The fused mass was then gradually heated and stirred until reaction commenced, and after a short time was allowed to cool. In all cases, the apparatus was surrounded by an inert gas.

The sulphides investigated were PbS, Cu₂S, SnS, CdS, ZnS, Sb₂S₃, Ag₂S, Bi₂S₃, NiS, and CoS, all of which were largely, and some completely, desulphurised by aluminium. Noteworthy is the reduction of zinc sulphide, to which is attributed a higher heat of formation than to the equivalent proportion of aluminium sulphide. With PbS, Cu₂S, SnS, Ag₂S, and Bi₂S₃, the amount of the metal obtained approximates closely to the theoretical quantity, whereas this is not the case either (1) with CdS and ZnS, owing to the volatility of the reduced metal, or (2) with NiS and CoS, owing to projection of material from the crucible in consequence of the excessive vigour of the reaction.

T. H. P.

New Synthesis of Phosgenite. W. A. HAMOR and H. E. GILL (*Amer. J. Sci.*, 1919, [iv], **47**, 430).—Phosgenite, PbCO₃.PbCl₂, has been synthesised by heating a mixture of lead hydroxide and excess of carbonyl chloride for one to four hours at 95°, 120°, 150°, 175°, 200°, and 250°. The best results were

obtained at 175° , the amount formed being less the higher the temperature above this value. The product was crystalline and of a faint yellow colour, identical in all respects with the naturally occurring mineral.

J. F. S.

Combinations of Mercuric Chloride and the Alkali Chlorides. C. TOURNEUX (*Ann. Chim.*, 1919, [ix], **11**, 225—361).

—From a study of the equilibrium of the system mercuric chloride—potassium chloride—water at 34° , 56° , 80° , and 100° , the author shows that it is possible to obtain two crystalline salts having the composition $\text{HgCl}_2 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$ and $2\text{HgCl}_2 \cdot \text{KCl} \cdot 2\text{H}_2\text{O}$. In addition, three sets of crystals have been obtained, the composition of which may be represented by $(2\text{HgCl}_2 \cdot \text{KCl} \cdot \text{H}_2\text{O})_4(\text{HgCl}_2 \cdot 2\text{KCl} \cdot \text{H}_2\text{O})$, $(2\text{HgCl}_2 \cdot \text{KCl} \cdot \text{H}_2\text{O})(\text{HgCl}_2 \cdot 2\text{KCl} \cdot \text{H}_2\text{O})$, and $(2\text{HgCl}_2 \cdot \text{KCl} \cdot \text{H}_2\text{O})(\text{HgCl}_2 \cdot 2\text{KCl} \cdot \text{H}_2\text{O})_4$.

The author is not certain as to whether the last three formulæ represent double salts or simply mixed crystals of the two salts the composition of which is expressed in the brackets. He has not succeeded in preparing the hydrate $2\text{HgCl}_2 \cdot \text{KCl} \cdot \text{H}_2\text{O}$. He has verified the existence at the ordinary temperature of the following crystalline salts: $\text{HgCl}_2 \cdot \text{RbCl} \cdot \text{H}_2\text{O}$; $\text{HgCl}_2 \cdot \text{NaCl} \cdot 2\text{H}_2\text{O}$; $\text{HgCl}_2 \cdot \text{NH}_4\text{Cl} \cdot \text{H}_2\text{O}$; $4\text{HgCl}_2 \cdot 3\text{RbCl} \cdot \text{H}_2\text{O}$.

The crystalline double salts formed by mercuric chloride and the alkali chlorides are all homœomorphic and show a marked chemical analogy. The analogy of the properties of these crystals with those of the zeolites suggest that the water content of the crystals depends on the vapour tension of the surrounding medium.

W. G.

Extraction of Gallium and Germanium from Zinc Oxide.

H. C. FOGG and C. JAMES (*J. Amer. Chem. Soc.*, 1919, **41**, 947—949).—Some zinc ores contain small, though appreciable, amounts of germanium and gallium, and, these metals being less volatile than zinc, remain behind in the retorts when the zinc distils off. These residues furnish a good source for the elements gallium and germanium, although the amounts obtainable vary enormously; for example, 100 lb. of one specimen gave 8 grams of pure gallium, whilst a second sample of 200 lb. yielded only the merest traces; the amount of germanium in the two samples was almost identical. One kilo. of the oxide prepared from the zinc residues was treated with 2400 c.c. of commercial hydrochloric acid in a large flask, the oxide being added in small portions to the acid to prevent caking. When all had dissolved, a little potassium chlorate was added carefully until, after vigorous shaking, oxides of chlorine were evolved. The flask was then connected to a condenser and a thermometer placed with its bulb in the liquid, and the liquid distilled; two fractions were collected, the first, up to 121° , containing very little germanium, and the second, up to 135 — 140° , containing practically the whole of the

germanium. The distillates from several quantities were then saturated with hydrogen sulphide, and the white sulphide filtered off. The liquid left in the flask was diluted with a litre of water and lead chloride allowed to settle. The clear liquid was decanted from the sediment and treated with ammonium hydroxide until a slight permanent precipitate was formed, metallic zinc was added, and the whole digested at the boiling point for several hours. The precipitation was considered complete when a portion of the supernatant liquid gave a precipitate of basic zinc chloride on dilution with water. The precipitated metals and basic salts were filtered off and the filtrate examined spectroscopically to ascertain if all the gallium had been precipitated. Ten such precipitates, corresponding with 30 kilos. of the original oxide, were united, dissolved in commercial hydrochloric acid with the aid of a little potassium chlorate, boiled, and lead chloride allowed to separate. This was removed and the solution saturated with hydrogen sulphide. The precipitate was filtered off and the filtrate boiled, neutralised with dilute ammonium hydroxide until a permanent precipitate just formed, and again digested with zinc at the boiling point. When the solution had turned basic, it was poured from the precipitate, diluted, and filtered, the operation being repeated with the filtrate until the basic precipitate ceased to show a gallium spectrum. The precipitates poor in gallium were placed with those first obtained from the crude zinc chloride. The precipitates rich in gallium were again dissolved in hydrochloric acid, the solution nearly neutralised, saturated with hydrogen sulphide, and filtered. The filtrate was treated with ammonium chloride, made alkaline to litmus with ammonia, and boiled until just acid. A gelatinous precipitate consisting of gallium, aluminium, and iron hydroxides was filtered off and washed. From 100 lb. of the crude zinc oxide, 60 grams of the mixture of hydroxides was obtained. These were dissolved in the minimum quantity of hydrochloric acid, diluted with water, and nearly neutralised with sodium hydroxide. After the addition of a little formic acid, the liquid was treated with an excess of sodium formate, the precipitate collected, and thoroughly washed to ensure the complete removal of zinc. The precipitate and filter paper were placed in water in a casserole, saturated with hydrogen sulphide, and digested with cold 1% hydrochloric acid. The insoluble tin and cadmium sulphides were removed by filtration. The filtrate was made slightly alkaline with ammonia, boiled until slightly acid, and the gallium and aluminium hydroxides filtered off. These were dissolved in the minimum quantity of hydrochloric acid, and an excess of sodium hydroxide solution added. The solution was then electrolysed by a current of 1.5 amperes, using platinum electrodes 3 cm. sq. The gallium was deposited on the cathode in bright, shining globules, which dropped off as they became larger. When no more gallium was deposited, the solution was poured off and the metal washed several times with water, and the globules then united by the addition of a few drops of concentrated hydrochloric acid.

J. F. S.

Monoclinic Double Selenates of the Iron Group. A. E. H. TUTTON (*Phil. Trans.*, 1919, [A], **218**, 395—440).—The crystallographic and optical investigation of the crystals of the four salts of the series $R_2M(SeO_4)_2 \cdot 6H_2O$, in which M is ferrous iron and R is potassium, rubidium, caesium, and ammonium, has been completed, and the detailed results are recorded in this paper. The examination of the crystals of the potassium salt was accomplished under great difficulties on account of the rapid decomposition of the crystals, apparently into the dihydrate, at temperatures very little above 0° . Suitable crystals were obtained on four very cold nights, and the necessary measurements were made by intensive working in a room the temperature of which never exceeded 6° .

The salts all crystallise in the holohedral class of the monoclinic system, and are closely isomorphous with the other salts of this extensive series. In this group, as in other groups of the series, there is a regular progression in the habit and dimensions of the crystals from the potassium, through the rubidium, to the caesium salt, whilst the ammonium salt approximates closely in most respects to the rubidium salt.

Potassium ferrous selenate, $K_2Fe(SeO_4)_2 \cdot 6H_2O$, $a:b:c=0.7490:1:0.5044$, $\beta=103^\circ 50'$, D_4^{20} 2.494, M.V. 210.39.

Rubidium ferrous selenate, $Rb_2Fe(SeO_4)_2 \cdot 6H_2O$, $a:b:c=0.7424:1:0.5000$, $\beta=104^\circ 57'$, D_4^{20} 2.800, M.V. 220.29.

Caesium ferrous selenate, $Cs_2Fe(SeO_4)_2 \cdot 6H_2O$, $a:b:c=0.7308:1:0.4979$, $\beta=106^\circ 2'$, D_4^{20} 3.048, M.V. 233.21.

Ammonium ferrous selenate, $(NH_4)_2Fe(SeO_4)_2 \cdot 6H_2O$, $a:b:c=0.7433:1:0.5019$, $\beta=106^\circ 9'$, D_4^{20} 2.191, M.V. 220.39.

The regular, progressive change in the dimensions of the crystal structure in the isomorphous series on passing from potassium to caesium is associated with the regular increase in the atomic number of the alkali metal. The isomorphism of the ammonium salts with those of the alkali metals is held to be proof of the invalidity of the Barlow-Pope theory of valency volume. E. H. R.

Triboluminescence of Uranium Compounds. J. A. SIEMSEN (*Chem. Zeit.*, 1919, **43**, 267).—The author has made experiments with a number of samples of uranium nitrate in an attempt to obtain explosive crystals of the kind reported by Ivanov (A., 1912, ii, 455) and Andrews (A., 1913, ii, 60). In no cases were explosive crystals obtained, but generally they showed the property of triboluminescence. It is concluded that the explosive crystals observed by the above authors owed their property to the presence of a labile nitric oxide compound. The triboluminescence of uranium salts is attributed to electrical tension in the crystals. E. H. R.

Analytical Chemistry.

The Use of Freezing-point Determinations in Quantitative Analysis. CHARLES EDWARD FAWSITT (T., 1919, 115, 801—808).

Calculation of Possible Error in Volumetric Analysis. V. ZOTIER (*Bull. Sci. Pharmacol.*, 1918, 25, 274—282, 357—364; from *Chem. Zentr.*, 1919, ii, 636—639).—A mathematical paper in which the inaccuracies inherent in volumetric analysis are considered. The errors arise from incorrect calibration and reading errors in measuring vessels (pipette and burette) and from uncertainty with respect to the end-point of the indicator. The various methods of preparing standard solutions are also treated, as well as errors due to impurity in the standard substance. A mathematical expression taking these factors into account is derived, for details of which the original must be consulted. It is thus calculated that the possible error in the determination of chlorine in commercial salt (1 gram of substance dissolved in 100 c.c. and titration of 20 c.c. of the solution with $N/10\text{-AgNO}_3$) is about 1 in 100.
H. W.

New and Rapid Apparatus for Electrochemical Analyses. J. T. KING (*Chem. and Met. Eng.*, 1919, 21, 25—29).—In electrochemical analyses, agitation of the electrolyte hastens deposition of the metal, and the author has originated a more efficient method of agitation by rotating the containing beaker. Two experimental designs and the final form of apparatus are described. Besides the method of stirring, the system of wiring and the electrode holders are novel. The circuit is not broken when a beaker is lowered and a cell removed from the circuit. The operation of the apparatus and the method of carrying out an analysis are described. Tests were made on copper solutions of known strength to determine the speed and accuracy of the apparatus, and the results are tabulated. With currents of three, six, and nine amperes, the times taken to deposit 1 gram of copper were found to be thirty-five, twenty-five, and sixteen minutes respectively. Three unknown brasses were analysed for copper, and the results obtained by this and other methods of stirring, and carried out by different operators, are tabulated, and show excellent agreement.
T. H. B.

Comparative Tests of "Palau" and "Rhotanium" Ware as Substitutes for Platinum Laboratory Utensils. L. J. GUREVICH and E. WICHES (*J. Ind. Eng. Chem.*, 1919, 11, 570—573).—"Rhotanium A" ware (gold, 90%; palladium, 10%) is superior to platinum as regards resistance to loss on heating, boiling hydrochloric and hydrofluoric acids, boiling 20% sodium hydr-

oxide solution, sulphuric acid, and fusion with sodium carbonate or potassium pyrosulphate, but inferior as regards the action of nitric acid, ferric chloride solution, and fused sodium hydroxide. It must not be heated higher than 1100°. "Rhotanium C" (gold, 70%; palladium, 30%) and "palau" (gold, 80%; palladium, 20%) alloys are superior to platinum as regards heating up to 1200°; they behave towards reagents similarly to "rhotanium A," but are not suitable for potassium pyrosulphate and sodium hydroxide fusions.

W. P. S.

Sulphite Leuco-derivatives of Triaminotriphenylmethane as Reagents for Alkalinity and for Dissociation of Salts.

I. GUARESCHI (*Gazzetta*, 1919, **49**, i, 115—123).—Magenta and other colouring matters of the triphenylmethane group, when reduced by means of sulphur dioxide or a hydrogen sulphite, serve as good reagents for bromine and hypobromites (A., 1912, ii, 989), and it is now found that they are also applicable to the detection of alkalinity, particularly with potable waters. The constitution of these compounds still remains undecided (compare Hantzsch and Ostwald, A., 1900, i, 256). The sensitiveness of the reaction is such that preliminary concentration of the water by evaporation is unnecessary; the intensity of the coloration is greater when an ethyl group than when a methyl group is present in the leuco-derivative, and still greater when the ethyl group is united to an imino-group.

Decolorised triethylrosaniline hydrochloride (Hofmann's violet) gives an intense violet coloration with dilute solutions of faintly alkaline salts, such as calcium hydroxide, carbonate or hydrogen carbonate, dimetallic hydrogen phosphates, borates, lead salts (normal or basic acetate), sodium acetate, basic quinine sulphate, aniline, magnesium phosphate, and magnesium ammonium phosphate; the reaction is more sensitive than that with litmus or other indicator. Wheat starch, which contains no proteins, gives no coloration, whereas rice starch, always containing more or less protein matter, reacts distinctly. The colouring matter formed is highly adherent to glass. With distilled water, or with dilute solutions of neutral salts like sodium chloride, no reaction takes place within an hour, and only a very faint coloration appears after a long time.

Similar colorations are given by magenta, *p*-rosaniline hydrochloride, methyl-violet, and crystal-violet, previously decolorised by sulphur dioxide. The coloration of the crystal-violet reagent by hypochlorites (compare Le Roy, A., 1916, ii, 535) is given also by solutions having an alkaline reaction, but free from hypochlorite.

T. H. P.

Estimation of Perchlorates, Alone, or in the Presence of Chlorates and Chlorides. J. GUILFOYLE WILLIAMS (*Chem.*

News, 1919, **119**, 8).—Perchlorates, but not chlorates, are reduced by titanium trichloride solution in hot acid solution. An

excess of titanium trichloride is used, and this excess is subsequently titrated with ferric sulphate solution. [See, further, *J. Soc. Chem. Ind.*, 1919, August.] W. P. S.

Estimation of Iodide in Mineral Waters and Brines. W. F. BAUGHMAN and W. W. SKINNER (*J. Ind. Eng. Chem.*, 1919, **11**, 563—568).—A quantity of the sample containing not more than 0.1 gram of iodine or more than 10 grams of total salts is diluted to 100 c.c., boiled with the addition of sodium hydroxide and sodium carbonate, and filtered. The filtrate is neutralised with sulphuric acid, 1 c.c. of 4% sodium hydroxide solution is added, the mixture boiled, an excess of potassium permanganate is added, and this excess then decomposed by treating the cold mixture with alcohol. After filtration, the solution is treated with 2 grams of potassium iodide, acidified with hydrochloric acid, and the liberated iodine titrated with thiosulphate solution. If it is desired to estimate bromine in the sample, the iodine may be first separated by steam distillation with the addition of ferric sulphate; the distilled iodine is collected in potassium iodide solution and titrated. W. P. S.

A Modified "Etching" Test for Fluorides. WILLIAM PARTRIDGE (*Analyst*, 1919, **44**, 234—235).—The substance under examination is treated with 2 or 3 c.c. of 25% (by volume) sulphuric acid, the liquid covered with a layer of butter fat, and the test-tube placed upright in water at 80° to 95° for three hours. In the presence of 0.01 gram of sodium fluoride, the glass in contact with the acid will be "etched," and the markings will not be affected by successive treatment with ether, boiling alcohol, and boiling hydrochloric acid, or by rubbing with a piece of wood. C. A. M.

Method of Analysis of Fluospar and of Basic Slags containing Fluorine. G. R. DOYLE (*Chem. News*, 1919, **118**, 304—305).—Half a gram of the finely powdered sample is weighed into a dish, converted into a paste with 5 c.c. of water, and evaporated on a water-bath almost to dryness with 35 c.c. of glacial acetic acid. A further quantity of 25 c.c. of glacial acetic acid is added, and the mass evaporated to dryness on a water-bath and then heated in a steam-oven until all acid has been expelled. The residue is transferred to a beaker and diluted to 80 c.c., boiled, and filtered. The filtrate contains (a) available lime (CaO or CaCO₃), (b) soluble silica, (c) manganese, (d) magnesia, (e) lead, whilst the residue contains (a) all calcium existing as CaF₂, (b) silica, and (c) iron and alumina. The residue is ignited in a platinum dish, cooled, weighed, treated with hydrofluoric acid, evaporated to dryness, ignited, and weighed. The loss in weight gives the amount of silica present. The remaining residue is treated with 5 c.c. of sulphuric acid and evaporated until fumes are evolved, then it is ignited and weighed. The gain in weight is the increase of calcium sulphate over calcium fluoride, $\text{CaSO}_4 \times 0.5735 = \text{CaF}_2$. The residue is boiled for twenty minutes

with 20 c.c. of hydrochloric acid, diluted, and precipitated by the addition of ammonium chloride and ammonia, boiled, filtered, ignited, and weighed. The weight is deducted from the weight of iron, aluminium, and calcium fluoride, and gives the weight of calcium fluoride. If lead is present, it must be removed by hydrogen sulphide before the iron and aluminium are precipitated. The filtrate is estimated in the usual way. J. F. S.

Estimation of the Oxygen Content of Organic Substances.

ROBERT STREBINGER (*Zeitsch. anal. Chem.*, 1919, **58**, 97—114).—Oxidation by heating at 200° with a mixture of potassium iodate and sulphuric acid, and subsequent iodometric titration of the excess of iodate, affords a means of estimating the oxygen content of organic substances provided that the percentage amounts of the other constituents are known. The method is applicable to substances containing carbon, hydrogen, oxygen, halogens, sulphur, and nitrogen, but the nitrogen must not be present as amide. The oxygen may be calculated from the following formula:

$$\text{O}\% = 2.6666 \times \text{C}\% + (1 - 0.21568 \times \text{N}\%/\text{H}\%) \times 7.9369 \times \text{H}\% + 1.497 \times \text{S}\% - 100 \times \text{O}'/E,$$

where E is the weight of substance and O' the quantity of oxygen yielded by the iodate; 6 molecules of iodate give 15 atoms of oxygen. W. P. S.

Estimation of Nitrogen and Ammonia as Ammonium Chloride. A. VILLIERS (*Bull. Soc. chim.*, 1919, [iv], **25**, 335—337. Compare A., 1918, ii, 332).—Further evidence is given showing that the loss in weight of ammonium chloride when heated in a narrow-necked, conical flask for four days at 105° is practically negligible (compare Auger, this vol., ii, 117). W. G.

Volumetric Estimation of Phosphoric Acid by the Pincus Method, as applied to the Estimation of Magnesium.

J. W. SPRINGER (*Zeitsch. angew. Chem.*, 1919, **32**, 192).—The magnesium salt is precipitated as ammonium magnesium phosphate, the precipitate heated to boiling with ammonium acetate solution and water, and titrated with standardised uranyl acetate solution, using potassium ferrocyanide as an external indicator. [See, further, *J. Soc. Chem. Ind.*, 1919, August.] W. P. S.

Microelementary Analysis. E. DIEPOLDER (*Chem. Zeit.*, 1919, **43**, 353—354).—Methods are described for the estimation of nitrogen, carbon, hydrogen, and halogens in very small quantities (a few mg.) of substance; the first three elements mentioned are estimated by combustion, whilst halogens are estimated by the Carius method. [See, further, *J. Soc. Chem. Ind.*, 1919, August.] W. P. S.

Micro-methods for the Determination of Carbon and Moisture in Minerals. G. KARL ALMSTRÖM (*Svensk. Kera. Tidskrift*, 1919, **31**, 71—74).—Pregl's apparatus for combustion

and his potassium dichromate were applied to the estimation of carbon dioxide and moisture in minerals. The moisture values obtained in this way were too high. Vanadium pentoxide, having a low m. p. (660°), being strongly acid at high temperatures and combining with most substances to give readily fusible products, was thought to be a likely substitute that might give better results. The results for carbon dioxide were accurate, but the moisture values were still too high. Twenty to thirty mg. of the sample were used, and to this was added 0.2 to 0.3 gram of the oxidising agent. Neither can be rendered sufficiently free from moisture to yield trustworthy results. A Penfield apparatus made on a "micro" scale gives trustworthy figures when employed in the estimation of moisture in minute amounts of mineral sample.

CHEMICAL ABSTRACTS.

Cyanometric Method of Estimating Silver and Halogens in Ammoniacal Solution. J. EGGERT and LOTTE ZEPFEL (*Ber.*, 1919, 52, [B], 1177—1185).—The procedure depends on the fact that silver iodide is only precipitated from very dilute ammoniacal solutions of silver salts by addition of potassium iodide when large amounts of electrolytes are present or when the solution is warmed, continuously shaken, or preserved for a long time; otherwise, an opalescence of colloidal silver iodide is formed. If potassium cyanide solution is added, the turbidity increases at first and suddenly disappears when the amount of CN' necessary for the formation of $\text{Ag}(\text{CN})'_2$ has been added. Silver is estimated in ammoniacal solution in the following manner. A known volume of approximately 0.1*N*-potassium cyanide solution is diluted with about four times its volume of water, and sufficient ammonia is added to make the solution at least 0.25*N*; after introduction of a quantity of potassium iodide approximately equivalent to that of the cyanide taken, the silver solution is added to incipient turbidity. Halogens are estimated indirectly by using an excess of silver nitrate solution and titration of the residual silver after filtration of the silver haloid. The method can also be applied for estimation of acids, the silver salts of which are distinguished by sufficient difference in their solubility in ammonia; thus, chloride and iodide may be simultaneously estimated in that their sum is determined by the indirect process and the iodide alone estimated in a solution which is sufficiently ammoniacal to retain the silver chloride in the dissolved state. To obtain accurate results, it is necessary that the amount of potassium iodide used as indicator should be approximately equivalent to the amounts of substance taken for titration.

The use of potassium iodide in Liebig's method of titration is shown to bring no advantage, and in certain cases even to lead to false results.

H. W.

Sensitive Reaction of Manganese Salts. H. CARON and D. RAQUET (*Ann. Chim. anal.*, 1919, [ii], 1, 174).—A red

coloration is obtained when 10 c.c. of a manganese salt solution is treated with 2 c.c. of saturated potassium oxalate solution, 1 c.c. of acetic acid, and a few drops of potassium hypochlorite solution. The test will detect the presence of as little as 0.05 mg. of manganese in 10 c.c. of solution. Zinc salts do not interfere with the reaction, but iron salts must not be present. W. P. S.

Estimation of Ferrous Iron by means of the Oxidation Potential. I. M. KOLTHOFF (*Chem. Weekblad*, 1919, **16**, 450—461).—The ferrous solution, acidified with sulphuric or hydrochloric acid, is titrated with a standardised potassium dichromate solution. The *E.M.F.* between a platinised platinum electrode immersed in the solution and a normal calomel electrode is determined after successive additions of the dichromate solution, and the values obtained are plotted in a curve against the volume of the solution added. In the neighbourhood of the end-point, the *E.M.F.* increases rapidly, the exact end-point being given by the middle point of the nearly vertical curve section. Titration with potassium bromate gives satisfactory results, the end-point being sharper in hydrochloric than in sulphuric acid solution. With potassium permanganate solution, the value of the *E.M.F.* obtained is variable, increasing when the liquid is stirred.

W. S. M.

Estimation of Nickel in Ferro-nickels and Steels. PAUL NICOLARDOT and GEORGES GOURMAIN (*Bull. Soc. chim.*, 1919, [iv], **25**, 338—344).—A comparison of the three methods of estimating nickel in nickel steels, namely: (1) electrolytic method; (2) precipitation with dicyanodiamidine; (3) precipitation with dimethylglyoxime. Method (2) gives results comparable with those of method (3), but needs much more care in its conduct. The results obtained by the use of dimethylglyoxime are invariably lower than by the electrolytic method, since in the latter method any cobalt present, and generally a little iron and manganese, are weighed in with the nickel. For rapid work, too, the dimethylglyoxime method is preferable, the precipitate being weighed on a tared filter paper. W. G.

Estimation of Small Quantities of Antimony. W. BEAM and G. A. FREAK (*Analyst*, 1919, **44**, 196—199).—When modified slightly, a method described by Schidrowitz and Goldsbrough (*A.*, 1911, ii, 338) was found to be trustworthy. In this method, the antimony is deposited on a strip of copper, then dissolved in alkaline permanganate solution, and estimated colorimetrically as sulphide. The chief modifications introduced are the reduction of antimony solution with sulphur dioxide before the precipitation with hydrogen sulphide (this ensures the precipitation of the metal as its trisulphide, which is always the case in the comparison solution), and the use of 1% potassium hydroxide solution and a limited amount of potassium permanganate solution for the solution of the

deposited antimony. [See, further, *J. Soc. Chem. Ind.*, 1919, 515A.] W. P. S.

Estimation of Small Amounts of Benzene in Ethyl Alcohol.

F. W. BABINGTON and ALFRED TINGLE (*J. Ind. Eng. Chem.*, 1919, **11**, 555—556).—One hundred c.c. of the alcohol are mixed with 200 c.c. of water and distilled, 20 c.c. of distillate being collected in a narrow, graduated tube having a capacity of 50 c.c. This distillate is treated with 15 c.c. of potassium dichromate solution (one-sixth saturated) and 2 c.c. of hydrochloric acid (D 1.12), the tube closed with a rubber stopper, and its contents mixed. After about fifteen minutes, the mixture is shaken with exactly 10 c.c. of light petroleum and the latter allowed to separate; the increase in volume of the petroleum gives the amount of benzene present. The method is trustworthy for quantities of benzene up to 0.75%.

W. P. S.

Chlorination of Benzene. Analysis of Mixtures of Benzene, Chlorobenzene, and Dichlorobenzene, etc.

PERCY F. FRANKLAND, S. RAYMOND CARTER, and DOROTHY WEBSTER (*J. Soc. Chem. Ind.*, 1919, **38**, 153—155).—The method described is similar in principle to that employed by Colman (A., 1915, ii, 184; *J. Soc. Chem. Ind.*, 1919, **38**, 57) for the estimation of the percentages of benzene, toluene, and xylene in commercial toluene. The sample (100 c.c.) is distilled from an Engler flask under uniform conditions, and the distillates are collected in measuring cylinders. Three fractions are obtained by interrupting the distillation at 122° (corr.) and again at 142° (corr.). The volumes of liquid which distil below 122° and above 142° are noted, and the percentages of benzene and chlorobenzene present in the original mixture are obtained from a graph which has been constructed from experiments with mixtures of known composition. The dichlorobenzene may be found by difference. The graph is only applicable to samples containing 50—80% of chlorobenzene and for those which contain such amounts of benzene and dichlorobenzene as yield not less than 5% or more than 50% either below 122° or above 142°; in cases where the sample does not fall within these limits, such measured volume of benzene, chlorobenzene, or dichlorobenzene is added that the resulting mixture comes within the specified limits. The graph was constructed by the use of pure *n*-dichlorobenzene, but it is found that the presence of *o*-dichlorobenzene does not materially affect the accuracy of the process even if it forms about 40% of the total dichlorobenzene present in the mixture. Benzene hexachloride, if present, should be filtered before distillation, and the quantity then remaining in solution is too small to influence the analysis; if its percentage is required, it is allowed to separate at the ordinary temperature from the fraction, b. p. above 140°, collected, washed with light petroleum (b. p. 65°), and dried. The mother liquor is concentrated, and the second crop similarly treated and weighed with the first lot of benzene hexachloride.

H. W.

Estimation of Monochlorobenzene in Mixtures containing Benzene, Monochlorobenzene, and Dichlorobenzene.

N. G. S. COPPIN and F. HOLT (*Analyst*, 1919, **44**, 226—229).—A method of estimating monochlorobenzene in crude chlorinated benzene has been based on Northall-Laurie's method of estimating toluene in commercial toluene (A., 1915, ii, 703). A known volume of the sample is distilled, the first quarter of the distillate collected, a further half then distilled, and the residual quarter left in the flask. The boiling points of the first fraction and of the residue are determined in the special apparatus devised by Northall-Laurie, and from these results, by reference to a graph constructed from the results obtained with mixtures of known composition, the amount of monochlorobenzene in the sample is found. The graph is made by plotting the results obtained with weighed quantities of benzene, monochlorobenzene, and *p*-dichlorobenzene, the boiling points of the first fractions forming the ordinates and those of the residues the abscissæ. Small amounts of *o*-dichlorobenzene and trichlorobenzene are also formed when benzene is chlorinated, but not in sufficient quantity to have a material influence on the results. [See, further, *J. Soc. Chem. Ind.*, 1919, August.]

C. A. M.

A Revision of the Copper Phosphate Method for the Titration of Sugar.

OTTO FOLIN and EUGENE C. PECK (*J. Biol. Chem.*, 1919, **38**, 287—291).—Variable results were encountered with this method when salt mixtures prepared from the same lot of chemicals by different individuals were employed. It was ascertained that, in order to obtain concordant results, great care must be taken to prepare the salt mixture correctly. The preparation of this mixture is described in detail. The method of Folin and McEllroy (A., 1918, ii, 207) could, however, be justly criticised on the ground that reduction of the copper sulphate by the thiocyanate may occur. By rendering the copper sulphate solution alkaline before adding the thiocyanate, this reduction is prevented. The modified process is as follows: 5 c.c. of the 5·9% copper sulphate solution are placed in a test-tube and rendered alkaline by the addition of 1 c.c. of saturated sodium carbonate. Four to five grams of the phosphate-carbonate-thiocyanate mixture are now added, and the whole is heated until the salts have dissolved. The titration is then carried out as described in the original method.

J. C. D.

Micro-estimation of Sugar in Blood.

A. KOWARSKY (*Deut. med. Woch.*, 1919, **45**, 188—190; from *Chem. Zentr.*, 1919, ii, 475).—The method depends on Bertrand's process, which consists in boiling the sugar solution with alkaline cuprous oxide solution, separating the precipitated copper oxide from the solution, and dissolving it in acidified iron sulphate solution; the ferrous oxide formed (equivalent to the cuprous oxide) is titrated with permanganate. To avoid loss when working with small quantities of

sugar, a known weight of the latter is added to the cuprous solution, which is subsequently deducted from that found experimentally. The method permits an exact estimation of sugar (to 0.01%) in 0.35 c.c. of blood, and can also be used for determining sugar in urine. It is particularly useful in diagnosis of disease of the kidneys, in which only small quantities of urine are frequently available; an exact estimation can be made with 0.1 c.c. of urine.

H. W.

New Method for the Estimation of Oxalic Acid. HUGO KRAUSE (*Ber.*, 1919, **52**, [B], 1222—1223. Compare this vol., ii, 203).—A reply to Ott (this vol., ii, 303).

H. W.

Methods for the Quantitative Estimation of Hippuric Acid. New, Simple, and Accurate Method. EDUARDO FILIPPI (*Arch. Farm. Sperim. sci. aff.*, 1918, **26**, 243—256; from *Chem. Zentr.*, 1919, ii, 472).—A review of the previous methods is given, but the results obtained by them are not satisfactory. A simple method has therefore been elaborated based on the observation of Pelouze, that hippuric acid is converted into benzoic acid when boiled with sulphuric acid and manganese dioxide. Urine (300—500 c.c.) is concentrated to 100 c.c. and extracted during two hours at 60—65° with a mixture of benzene (2 volumes) and alcohol-free ether (1 volume); after removal of the solvent, the residue is heated under a reflux condenser, gently at first, but finally more strongly, with sulphuric acid (20 c.c.) and manganese dioxide (3—4 grams) during one and a-half hours. The product is distilled with steam, and the distillate is thoroughly extracted with ether. The benzoic acid left after removal of the ether is weighed.

H. W.

Micro-estimation of Fat. E. and (MRS.) F. WEEHUIZEN (*Pharm. Weekblad*, 1919, **56**, 810—822).—A criticism of the method of Ivar Bang for the estimation of fat in small quantities of blood (*Methoden zur Mikrobestimmung einiger Blutbestandteile*). The following improvement of the method is proposed: About 0.3 gram of blood is absorbed in two or three pieces of filter paper (16 mm. × 26 mm.), and the weight determined in a torsion balance. The papers are dried in a vacuum and then placed in a test-tube (2.5 cm. × 16 cm.) with about 7 c.c. of alcohol. The tube is suspended in a water-bath at 90°, and the alcohol boiled for five minutes. The solution is transferred to a pointed centrifuge tube (1.5 × 10 cm.) and evaporated to 2.5 c.c. in a water-bath. The papers are extracted again with 8 c.c. of alcohol, and the solution is added to the centrifuge tube, in which the volume is again reduced to 2.5 c.c. In both cases, evaporation is expedited by passing hydrogen through a capillary tube into the liquid. Five drops of *N*/2-sodium hydroxide solution are now added, and the evaporation is continued until the volume is reduced to 0.3 c.c. As the duration of the saponification must be at least twenty

minutes, it may be necessary to add ten drops of alcohol and a drop of water when a volume of 1 c.c. is reached. The residue, which must be free from alcohol, is made up to 5 c.c. and is transferred to a micro-burette. The solution is used to titrate 1 c.c. of the standard calcium chloride solution until a permanent froth is obtained. The standard solution is prepared by adding 5.9 c.c. of *N*/10-calcium chloride solution to 13 grams of sodium chloride and making up to 1 litre. One c.c. of this solution is equivalent to 0.312 mg. of triolein.

W. S. M.

Schiff's Reaction for the Detection of Carbamide.

DOMENICO GANASSINI (*Arch. Farm. speriment. sci. aff.*, 1918, **26**, 238—242; from *Chem. Zentr.*, 1919, ii, 473).—Schiff's reaction does not occur with pure furfuraldehyde. Acetone was found to be the active constituent of an efficient sample of furfuraldehyde. The reaction is obtained with certainty with a reagent of the following composition: furfuraldehyde (5 drops), acetone (2 c.c.), water (2 c.c.), and concentrated hydrochloric acid (1 c.c.). When a small quantity of this reagent is added to a minimal amount of carbamide, a pink coloration is gradually developed which becomes red and then intensely purple, and later brown. If acetone is replaced by other substances containing the COMe-group, such as ethyl acetate, acetaldehyde, acetylacetone, or pyruvic acid, red to violet colorations are more or less slowly developed, which, however, are indefinite and not to be compared with the beautiful coloration in the presence of acetone.

H. W.

Estimation of the Amyolytic Power of Saliva. L.

GRIMBERT (*J. Pharm. Chim.*, 1919, [vii], **19**, 244—250).—A quantity of air-dried potato starch equivalent to 5 grams of dry starch is boiled for two minutes with 100 c.c. of water, then cooled, 4 c.c. of filtered saliva are added, and the mixture is kept at 37° for one hour; it is then heated at 100° for ten minutes, cooled, diluted to 200 c.c., filtered, and the maltose is estimated in the filtrate. The amount of maltose is multiplied by 0.9473 to give the quantity of starch saccharified, and this, expressed as a percentage of the total starch, gives the amyolytic power of the saliva; for normal saliva, it lies between 73 and 74.

W. P. S.

Value of Some New Colour Reactions of Urine. ALEX.

SKUTETZKY and M. KLAFTEN (*Wien. klin. Woch.*, 1918, **31**, 1016—1018; from *Chem. Zentr.*, 1919, ii, 8).—The reactions proposed by Russo (methylene-green reaction), Wiener, and Kronberger have been critically examined; in each case, the coloration observed is due to simple physico-chemical causes, and does not depend on chemical processes. The reactions are consequently without diagnostic value.

H. W.

General and Physical Chemistry.

The Infra-red Spectrum of Iron. H. M. RANDALL and E. F. BARKER (*Astrophys. J.*, 1919, **49**, 42—47).—The region investigated extended from 9000 to 30,000 Å., and was found to contain some fifty measurable lines. The experimental arrangement was the same as that previously described (Randall, A., 1910, ii, 1014). The slit of the collimator and the thermopile were at first approximately 0.2 mm. wide, and covered a region in the neighbourhood of 1μ of about 6 Å. and at 3μ of about 3.7 Å. Later the entire spectrum was examined with a slit 0.5 mm. wide, and a very appreciable number of weaker lines were found and measured. No systematic differences between the values of wave-lengths measured with the slits of different width were noted. The material used in the major part of the work was ingot iron (99.8% Fe), the largest single impurity being copper, approximately 0.04%. Electrolytic iron also was used. No lines due to impurities in either were observed. The iron was placed in a boring in the positive carbon (1.9 cm.), the hole being as large as the carbon would permit. The carbons showed several infra-red potassium lines and also two others, the approximate values of which are 11,439 Å. and 10,692 Å. The origin of these lines is not known. The current used was in general greater than 60 amps. Tables of wave-lengths are given in Angström units, as measured in air according to the Rowland scale. The relative intensities of the lines were estimated from the galvanometer deflexions. For the region between 0.8μ and 1μ the photographic method is more sensitive than the bolometric, but beyond 1μ the latter becomes increasingly the more sensitive.

CHEMICAL ABSTRACTS.

The Infra-red Spectra of Cobalt, Nickel, Manganese, and Chromium. H. M. RANDALL and E. F. BARKER (*Astrophys. J.*, 1919, **49**, 54—60. Compare preceding abstract).—The experimental arrangement and methods were the same as those for the iron spectrum. With the exception of manganese, which volatilised readily and gave a comparatively steady arc, the metals were very similar to iron in their action in the arc. Nickel and cobalt produced possibly an even more uncertain arc than iron. The strongest lines were given by manganese. The materials used were "pure" metals of commerce. No lines due to any of the impurities likely to be found were actually observed. The currents used were 60—80 amps. The spectrum of each metal was in general searched twice, once with narrow slits and once with double width slits. A number of the lines in the tables are multiples of strong lines of short wave-lengths. It is thought, however, that in each case it has been established that the higher order line of short wave-length is superposed by a line of long wave-length of the first order.

CHEMICAL ABSTRACTS.

The Applications of Beer's Law in Organic Chemistry.

E. J. E. HÜFFER (*Chem. Weekblad*, 1919, **16**, 720—734).—A discussion of Beer's law of light absorption and its application to the determination of various cases of isomerism and polymerism in organic chemistry. Special reference is made to the colour theory of Hantzsch.

W. S. M.

The X-Ray Spectra of the Elements. M. DE BROGLIE (*Compt. rend.*, 1919, **169**, 134—136).—The author has measured the frequency difference of the α - and β -rays in the K -spectrum of rhodium, and from these values has calculated the fundamental frequency of interval of Sommerfeld (*Ann. Physik*, 1916). He obtains the value $\Delta\nu_H = 0.369$, which is in close agreement with Paschen's figure (*loc. cit.*).

He has measured the wave-lengths of the first two L -bands in the absorption spectrum of radium, the results being: band L_1 , $\lambda = 0.802 \times 10^{-8}$ cm.; band L_2 , $\lambda = 0.670 \times 10^{-8}$ cm. The latter figure is a correction of one previously given (compare this vol., ii, 207).

W. G.

Relation between General X-Radiation and the Atomic Number of the Target.

W. DUANE and T. SHIMIZU (*Physical Rev.*, 1918, **11**, 491—492).—The intensity of the general X-radiation is proportional to the atomic number, and not to the atomic weight of the radiator. The apparatus used was a rotating target on which were mounted quadrants of iron, cobalt, nickel, and copper. The current produced by ionisation in a chamber containing methyl iodide was:

Volts.	Ion-current (volts/sec.).			
	Cu (29).	Ni (28).	Co (27).	Fe (26).
19,140	0.0124	0.0120	0.0114	0.0110
32,400	0.1327	0.1295	0.1251	0.1210

The numbers in parentheses are the respective atomic numbers. Cobalt occupies a position between iron and nickel, according to its atomic number as determined by Moseley, but not according to its atomic weight, which is anomalous.

CHEMICAL ABSTRACTS.

The Structure of Radioactive Elements.

INGO W. D. HACKH (*Physical Rev.*, 1919, **13**, 165—170).—Partial atomic structures of the elements in the periodic table between uranium and lead, on the basis of the radioactive disintegration series, are suggested. The emission of the α -particle causes the change of position of two electrons from the valency ring to an interior unstable ring, and the emissions of the β -particle the change of one electron in the opposite sense. This is referred to as a theory of metastatic electrons, and it supports the view that the seat of disintegration is not in the outer or valency shell, but in the next inner shell, and is caused by the shifting of two electrons.

F. S.

"Old Age" of Chemical Elements. INGO W. D. HACKH (*Science*, 1919, **49**, 328—329).—A discussion based on Richards'

work on radioactive lead (A., 1914, ii, 453; 1917, ii, 91). The author states that "all other elements should be subject to an increase in mass, and it could therefore be predicted that, for example, helium of the atmosphere and of minerals will have an 'atomic weight' which is 0.0214 higher than the atomic weight of helium from radioactive disintegration, that is, there should be an 'old' or 'common' helium with atomic weight of about 3.94, and a 'neo' helium of atomic weight 3.92."

CHEMICAL ABSTRACTS.

Phenomena of Electrolytic Luminescence shown by certain Metallic Anodes. I. JAMES LAVAUX (*Compt. rend.*, 1919, 169, 180—182).—Certain metals capable of giving, with the electrolytic anion, insoluble, adherent salts, which are non-conductors, show luminous phenomena correlative with a state of intense anodic polarisation. Of the metals studied, iron, copper, cadmium, and lead do not show any luminous phenomena and show no tendency to anodic polarisation. On the other hand, aluminium, magnesium, zinc, and bismuth show both. The luminous phenomena may be of two types, namely, phosphorescence and sparking. The first three metals show both types, but bismuth only shows sparking. The phenomena of electrolytic phosphorescence only appear in very short electric fields of high intensity, and are connected with high polarisation of the anode and the creation at its surface of an intense electric field. The phosphorescence is not accompanied by noise or sparking, and only occasions a minute expenditure of current and a very feeble development of heat. On the other hand, the sparking appears to characterise an abnormal working of the apparatus. It occurs in two forms: (1) more or less numerous, small, brilliant sparks; (2) a rain of fire giving the anode the appearance of a star-spangled sky in a state of continuous transformation. The sparking is due to the momentary rupture of the isolating layer at points where, for a few moments, a current sufficiently intense to volatilise a liquid film passes, whence interruption, sparking, and crepitation.

Of the four metals exhibiting these phenomena, aluminium is the best for their study.

W. G.

The Melting Points of Mixtures of Organic Compounds. RICHARD MEYER and WILHELM MEYER (*Ber.*, 1919, 52, [B], 1249—1255).—The melting point of an organic compound is, in general, depressed by admixture with a second substance; the authors have previously shown that this is not the case with the tribromo-compounds of mesitylene and ψ -cumene (this vol., i, 72), and now describe a series of similar observations with the following compounds: tetrabromo-*o*-xylene and tetrabromo-*m*-xylene; tetrabromo-*m*-xylene and tetrabromo-*p*-xylene; tetrabromo-*o*-xylene and tetrabromo-*p*-xylene; tetrabromo-*o*-, -*m*-, and -*p*-xylenes; dibromodurene and dibromoisodurene; thiophen picrate and thionaphthen picrate; thionaphthen picrate and naphthalene picrate; thiophen

picrate and naphthalene picrate; α - and β -methylnaphthalene picrates; β -methylnaphthalene and naphthalene picrates; mono-chloro- and monobromo-hydroxyhydrindenes. The phenomena have been more exhaustively investigated with the methylnaphthalene picrates and with naphthalene and β -methylnaphthalene picrates. The melting points of synthetic mixtures were determined in capillaries on the one hand and by determining the temperature of solidification on the other, similar, but not identical, results being obtained by either method. In the case of naphthalene and β -methylnaphthalene picrates, a depression is not observed, but the melting point rises sharply when more than 33% of the former is present; with α - and β -methylnaphthalene picrates, a slight depression occurs until the concentration of the former attains about 16%, after which the melting point rises. In both cases, the authors consider that mixed crystals are formed. H. W.

A Modification of the Freezing-point Method for the Determination of Molecular Weights. H. J. PRINS (*Chem. Weekblad*, 1919, **16**, 929—931).—The determination of the molecular weight of substances containing hydroxyl by means of the depression of the freezing point in benzene solution is rendered difficult owing to the association of the solute. In such cases, a number of freezing-point measurements are made, each after successive additions of about 2 c.c. of benzene from a burette. The degree of association decreases with increasing dilution, and the true molecular weight is easily obtained by graphical extrapolation. W. S. M.

A New Form of Distilling Bulb. J. S. MCHARGUE (*J. Ind. Eng. Chem.*, 1919, **11**, 670—671).—A new form of distilling bulb can be made from sections of glass tubing of different diameter. A bulb is blown on the end of the larger tube, and in the base of this a hole is blown to receive the top of the smaller tube, which has been made in the form of a T-tube with its arms open and deflected downwards. This is sealed into the tube, two small openings being left near the ends of the T-piece to allow condensed water to flow back into the interior of the distilling flask. The other end of the larger tube is bent twice at right angles, and is connected with the condenser. By the use of this bulb, soap bubbles are broken up, and the contents of the distilling flask cannot be carried over mechanically. A further advantage is that the steam issuing from the two ends of the T-piece into the bulb keeps the latter at a uniform temperature and accelerates the distillation. C. A. M.

The Density of the Saturated Vapour of Propyl Acetate and the Density of the Liquid which Emits this Vapour. E. ARIÈS (*Compt. rend.*, 1919, **169**, 216—219).—In the formulæ previously given for the molecular volumes of the saturated vapour and the liquid which emits it (see this vol., ii, 184), the values of the function a were not known. The author now deduces a formula

for calculating the values of a , and by means of it calculates the values of v_1 and v_2 for propyl acetate over a temperature range from 90° to 276.2° . The results are in close accord with those observed by Young.

W. G.

The Use of Turpentine Resin in Turpentine as a Foam Breaker. E. C. KENDALL (*J. Biol. Chem.*, 1919, **38**, 529).—A 20% solution of resin in turpentine is a most efficient foam breaker. The solution should be neutral to alizarin.

J. C. D.

Equilibrium in the System $\text{Na}_2\text{SO}_4\text{--CuSO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$. H. W. FOOTE (*J. Ind. Eng. Chem.*, 1919, **11**, 629—631).—At a given temperature, univariant systems of three components have two solid phases in equilibrium with a solution of definite composition and vapour pressure, whilst in the case of systems of four components there are three solid phases at such points. To determine the univariant points in systems of three components, a series of crystallisations at the given temperatures was made. When one compound was deposited near the point where another was formed an excess of the latter, or in some cases of both compounds, was added, and the solubility of the mixture determined. After the univariant points in a ternary mixture had been obtained, the corresponding points in a quaternary mixture were found by adding an excess of the third solid. In determining the changes which take place when sulphuric acid is added in increasing amounts, up to 60%, to the system $\text{Na}_2\text{SO}_4\text{--CuSO}_4\text{--H}_2\text{O}$, the solubilities of the univariant systems were determined, and the points graphically represented were connected with straight lines to show the composition of the corresponding bivariant systems. In the case of solutions containing the four components, copper was estimated electrolytically, sodium as sulphate after removal of the excess of sulphuric acid by ignition with ammonium carbonate, and free sulphuric acid by titration with sodium hydroxide solution.

System $\text{Na}_2\text{SO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$.—The results obtained at 25° agreed substantially with those of D'Ans (A., 1906, ii, 351), although no evidence of the formation of the hydrate, $\text{Na}_3\text{H}(\text{SO}_4)_2\cdot\text{H}_2\text{O}$, which D'Ans found to be rarely formed, was obtained. At 12° , the following compounds separated: $\text{Na}_2\text{SO}_4\cdot 10\text{H}_2\text{O}$, $\text{Na}_2\text{SO}_4\cdot 10\text{H}_2\text{O}$ and $\text{Na}_3\text{H}(\text{SO}_4)_2$, $\text{Na}_3\text{H}(\text{SO}_4)_2$ and $\text{NaHSO}_4\cdot\text{H}_2\text{O}$, $\text{NaHSO}_4\cdot\text{H}_2\text{O}$. At 25° , the solubility relationships are more simple, for at 12° the anhydrous salt is not stable under any conditions, and the decahydrate exists in equilibrium with the salt $\text{Na}_3\text{H}(\text{SO}_4)_2$ at the univariant point (see also Pascal, A., 1917, ii, 248).

System $\text{CuSO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$.—In this system no acid salt is formed, but the sulphuric acid dehydrates the pentahydrate, yielding successively the trihydrate, monohydrate, and, finally, the anhydrous salt, in concentrated sulphuric acid.

System $\text{Na}_2\text{SO}_4\text{--CuSO}_4\text{--H}_2\text{O}$.—A transition temperature was observed at 16.7° , below which only a single salt crystallised. At 12° there is only a univariant system with two solid phases,

$\text{Na}_2\text{SO}_4, 10\text{H}_2\text{O}$ and $\text{CuSO}_4, 5\text{H}_2\text{O}$. At 25° there are two such systems, in one of which the solid phases consist of the double salt $\text{Na}_2\text{SO}_4, \text{CuSO}_4, 2\text{H}_2\text{O}$ and $\text{CuSO}_4, 5\text{H}_2\text{O}$, whilst in the other they consist of the double salt and $\text{Na}_2\text{SO}_4, 10\text{H}_2\text{O}$.

System $\text{Na}_2\text{SO}_4\text{--CuSO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$.—At 12° the two salts in water crystallise separately, but when more than 7.4% of sulphuric acid is present, the double salt forms, and at this concentration the univariant system contains the three solid phases of the two single salts and the double salt. In the presence of this proportion of sulphuric acid, the double salt is stable below its transition temperature. Equilibrium in the system $\text{CuSO}_4, 5\text{H}_2\text{O}$ — $\text{Na}_2\text{SO}_4, 10\text{H}_2\text{O}$ —double salt is reached very slowly at 12° , and the two single salts can remain in contact with a solution containing more than 7.4% of sulphuric acid for a considerable time without forming the double salt. The other systems soon attained equilibrium. At 12° the solid phases were as follows: (1) $\text{Na}_2\text{SO}_4, 10\text{H}_2\text{O}$, $\text{Na}_3\text{H}(\text{SO}_4)_2$, double salt with 16.50% sulphuric acid in solution. (2) $\text{Na}_3\text{H}(\text{SO}_4)_2$, $\text{NaHSO}_4, \text{H}_2\text{O}$, double salt with 27.97% sulphuric acid. (3) $\text{NaHSO}_4, \text{H}_2\text{O}$, double salt (bivariant) with 58.2% sulphuric acid. (4) $\text{CuSO}_4, 5\text{H}_2\text{O}$, $\text{CuSO}_4, 3\text{H}_2\text{O}$, double salt with 50.54% sulphuric acid. (5) $\text{CuSO}_4, 3\text{H}_2\text{O}$, $\text{CuSO}_4, \text{H}_2\text{O}$, double salt with 59.96% sulphuric acid. (6) $\text{Na}_2\text{SO}_4, 10\text{H}_2\text{O}$, $\text{CuSO}_4, 5\text{H}_2\text{O}$, double salt with 7.40% sulphuric acid. The results obtained at 12° and 25° are plotted in diagrammatic form, and show the instability of the sodium hydrogen sulphates in presence of copper sulphate, which converts them into the double salt.

C. A. M.

Action of Sulphuric Acid on certain Organic Compounds of Homologous and Isomeric Series. JAROSLAV MILBAUER and ANTONÍN NĚMEC (*J. pr. Chem.*, 1919, [ii], **99**, 93—105).—The authors have made experiments to ascertain the influence exerted by the constitution of organic compounds on the velocity of their oxidation by sulphuric acid. In each case, 4×10^{-4} gram-mols. of the compound were heated with 25 c.c. of the concentrated acid, this giving a column of liquid 9.5 cm. in height. The temperature was usually kept at 200° , but in some cases in which the velocity of reaction was very low, temperatures as high as 290° were employed. The sulphur dioxide formed was expelled by means of a current of carbon dioxide and its amount determined.

The aldoses are more difficult to oxidise than the corresponding polyhydroxy-derivatives, with the exception of mannitol, which in very small amounts (0.00004 mol.) retards the combustion of carbohydrates, without, however, affecting the final stage reached; mannitol thus acts as a true negative catalyst. The methylated carbohydrates undergo more profound combustion than the corresponding aldoses or alcohols containing the same number of carbon atoms; increase in the number of hydrogen atoms united to a carbon atom is accompanied by increase in the amount of sulphur dioxide formed. With isomeric sugars, steric configuration has no

influence on the combustion, and with di- and tri-saccharides, although these are not completely burnt, the amount of sulphur dioxide formed is equal to the sum of the amounts yielded by the constituent monosaccharides; the latter also do not undergo complete combustion. Mercuric sulphate not only acts as a positive catalyst, but increases the total quantity of sulphur dioxide; with 0.0001 gram-mol. of the salt, the increase amounts to 9% in the case of sucrose.

Dicarboxylic acids of the type $\text{CO}_2\text{H}\cdot[\text{CH}_2]_n\cdot\text{CO}_2\text{H}$ give with sulphuric acid at 200° only small amounts of sulphur dioxide, this resulting from decomposition of the acids with formation of carbon dioxide and monoxide, followed by reaction of the latter with the sulphuric acid, $\text{CO} + \text{H}_2\text{SO}_4 = \text{CO}_2 + \text{SO}_2 + \text{H}_2\text{O}$.

The unsaturated acids are very easily attacked, scission occurring first at the double linking. Aliphatic acids, such as oleic and fumaric acids, are oxidised far more rapidly than aromatic acids like cinnamic acid; aromatic hydroxy-acids (salicylic) are not oxidised by sulphuric acid at 200° . With the dicarboxylic acids of the aliphatic series, neither the velocity of combustion nor the amount of sulphur dioxide formed depends on the number of hydroxy-groups in the molecule, the reaction being determined in each case by the special chemical structure of the acid; here also mannitol acts as a true negative catalyst, whilst mercuric sulphate not only accelerates the oxidation, but carries it to a further extent.

With the amino-acids, the quantity of sulphur dioxide formed and the velocity of the combustion increase with the molecular weight; mannitol, and also boric anhydride, act as negative catalysts, and mercuric sulphate exerts the action described above. In the case of the aromatic hydrocarbons, the combustion proceeds further as the number of carbon-containing groups attached to the benzene nucleus increases.

Of the dihydroxybenzenes, the para-compound is oxidised the most rapidly and the meta-compound the most slowly, this behaviour being analogous to the reducing powers of these compounds when employed as photographic developers. None of the trihydroxybenzenes is oxidised as rapidly as it would be if one of the three hydroxy-groups were removed, but the rule holding with the dihydroxy-derivatives is obeyed; thus, pyrogallol represents a combination of two ortho-positions, hydroxyquinol one of an ortho and a meta-position, and phloroglucinol one of two meta-positions. α -Naphthol is more rapidly oxidised than β -naphthol. With the quinones, the combustion is the more rapid the smaller the number of substituent groups in the $\text{O}:\text{C}_6\text{H}_4:\text{O}$ nucleus. T. H. P.

Derivation of the Law of Even Atomic Numbers. ERNST MOHR (*J. pr. Chem.*, 1919, [ii], 99, 106—108).—If in any molecule the numbers of uni-, bi-, . . . sexa-valent atoms are a , b , . . . f respectively, the sum of all the valencies is given by $\Sigma V = a + 2b + 3c + 4d + 5e + 6f$. On the assumption that no valency in the mole-

cule remains unsaturated, the sum of all the linkings in the molecule is represented thus: $\Sigma B = \Sigma V/2 = b + 2d + 3f + (a + 3c + 5e)/2$. Since both ΣB and $(b + 2d + 3f)$ are positive integers, the term $(a + 3c + 5e)/2$ must also be a positive integer. Further, as $(c + 2e)$ is a positive integer, the expression $(a + 3c + 5e)/2 - (c + 2e)$, that is, $(a + c + e)/2$, must also be a positive whole number, and $(a + c + e)$ a positive, even integer; this is the law of even atomic numbers. A similar proof holds for the case when septa- and octa-valent atoms are present in the molecule.

With substances like triphenylmethyl, $C_{19}H_{15}$, in the molecule of which one valency is unsatisfied, the law holds only if one of the carbon atoms is regarded as tervalent.

This law is often useful in indicating the possibility or otherwise of particular molecular formulæ.

T. H. P.

Inorganic Chemistry.

The Solubility of Iodine in Water-Alcohol Mixtures. N. SCHOORL and A. REGENBOGEN (*Pharm. Weekblad*, 1919, **56**, 538—545).—The results of solubility determinations of iodine in water-alcohol mixtures as given in the literature are generally much too high, on account of the formation of hydriodic acid during the prolonged contact of the iodine with the solvent. The authors eliminate this source of error by preparing a nearly saturated solution of iodine in absolute alcohol. A weighed quantity of this is mixed with a weighed quantity of water, and, after shaking, a portion of the solution is drawn through a filter into a pipette and weighed. Potassium iodide solution is added and the iodine titrated with thiosulphate. W. S. M.

Effect of a Film of Oil on the Aeration of Water. HERBERT F. STEPHENSON (*Analyst*, 1919, **44**, 288).—Water covered with a layer of petroleum oil 0.6 cm. in depth absorbs oxygen from the atmosphere at the same rate as does water not covered by oil. W. P. S.

Fluorosulphonic Acid, Fluorosulphonates, and Sulphuryl Fluoride. WILHELM TRAUBE, J. HOERENZ, and F. WUNDERLICH (*Ber.*, 1919, **52**, [B], 1272—1284).—It has been previously shown that ammonium fluorosulphonate can be prepared by the action of sulphur trioxide on ammonium fluoride (*A.*, 1913, ii, 947); the further investigation of this and similar substances is described in the present communication.

Ammonium fluorosulphonate is most conveniently prepared by the gradual addition of dry ammonium fluoride to sulphuric acid

containing about 70% of sulphur trioxide, and treatment of the product with a small excess of ammonia dissolved in methyl alcohol. The salt has m. p. 245° and readily reacts with gaseous ammonia, particularly at low temperatures, with formation of liquid amines. The alkali fluorosulphonates are prepared by the action of the requisite alkali hydroxide on the ammonium salt in aqueous solution; the *potassium* salt, short, stout prisms, m. p. 311° , the *rubidium* salt, m. p. 304° , the *lithium* salt, long, shining needles ($+3\text{H}_2\text{O}$), m. p. $60-61^{\circ}$ or m. p. about 360° (anhydrous), are described. All the fluorosulphonates are freely soluble in water, with the exception of the *nitron* salt. The *barium* salt was not obtained in the pure form. The fluorosulphonates are unexpectedly stable towards water, from which they can be crystallised if the operation is rapidly performed; in the presence of mineral acids, they are readily hydrolysed to hydrofluoric and sulphuric acids, but are much more stable in alkaline solution. With aqueous ammonia, they yield chiefly aminosulphonates (compare this vol., i, 434).

The alkali fluorosulphonates are very stable towards heat; thus, when the potassium salt was heated for some time to bright redness, it only suffered slight decomposition, with the evolution of sulphur dioxide, sulphur trioxide, hydrogen fluoride, and oxygen. Crude barium fluorosulphonate, on the other hand, is decomposed at a red heat into barium sulphate and sulphonyl fluoride, this being the most convenient method of preparing the latter.

The formation of fluorosulphonates by heating mixtures of fluoride and pyrosulphates has been further investigated; the best yields are obtained from potassium pyrosulphate and an excess of ammonium fluoride; the yield is appreciably less when the latter is replaced by potassium fluoride, and still poorer when sodium fluoride is used. Fluorosulphonates are also obtained by heating mixtures of ammonium persulphate with fluoride, or by compressing fluoride and pyrosulphate, particularly in the presence of a little water. H. W.

Reaction of Thiosulphate with Iodine. I. M. KOLTHOFF (*Pharm. Weekblad*, 1919, **56**, 572—585).—In neutral or weakly acid solution, the reaction between iodine and thiosulphate takes place according to the equation $2\text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2 = \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI}$. In weakly alkaline solutions, part of the thiosulphate is oxidised directly to sulphate without the intermediate formation of tetrathionate. The side reaction may be represented in two stages: $\text{I}_2 + \text{OH}' = \text{HOI} + \text{I}'$, followed by $4\text{HOI} + \text{S}_2\text{O}_3'' + 6\text{OH}' = 2\text{SO}_4'' + 4\text{I}' + 5\text{H}_2\text{O}$. In sufficiently strongly alkaline solution, all the thiosulphate may in this way be oxidised to sulphate. In strongly acid solution, the reaction is as in neutral solution, the decomposition of the thiosulphate by the acid being slow in comparison with the formation of tetrathionate. W. S. M.

Electrolytic Preparation of Colloidal Selenium. A. GUTBIER and G. L. WEISE (*Ber.*, 1919, **52**, [B], 1374—1378).—When a dilute, aqueous solution of selenium dioxide is electrolysed

between platinum poles (preferably in the presence of a trace of alkali) with a tension of 220 volts, a moderate evolution of gas which does not contain hydrogen selenide is first observed; as soon, however, as the solution attains its boiling point, the formation of colloidal selenium commences, and the solution becomes consecutively yellow, yellowish-red, red, bluish-red, and finally blue. Selenium is not deposited in an irreversible form until the latter stage is reached provided that the original solution is not too concentrated. The yellow systems become yellowish-red when cooled, and can be preserved, even if not dialysed; they can readily be purified by dialysis, are not decomposed by filtration through paper, and can be considerably concentrated by evaporation over a free flame. The yellowish-red solutions sometimes retain their colour and at other times become red when cooled; in the former case, they can be purified by dialysis, and then behave in the same manner as the yellow solutions. The red solutions invariably show a tendency to become bluish-red when cooled—a sign of incipient coagulation; they can only be obtained in a moderately stable condition if dialysed while still hot, and then immediately diluted with pure water or with a solution of a protective colloid, such as gum arabic. The bluish-red and the blue solutions decompose generally when cooled, invariably during dialysis or when preserved at the ordinary temperature. All the dialysed solutions are very sensitive towards electrolytes; red precipitates are thus obtained which pass into the black or grey modification of selenium when heated with the solution of the electrolyte.

H. W.

Bibliography of Helium Literature. E. R. WEAVER (*J. Ind. Eng. Chem.*, 1919, **11**, 682—688).—A bibliography of the literature connected with helium is given, including everything of scientific interest up to January, 1919. It is classified under the following headings: Discovery and Identification; Occurrence of Helium; Formation of Helium; Separation and Purification; Properties; Liquefaction and Properties of Liquid Helium; Applications of Helium; and Miscellaneous.

C. A. M.

The Stability of the Sulphones formed by the Iodides of Sodium, Rubidium, and Cæsium. R. DE FORCRAND and F. TABOURY (*Compt. rend.*, 1919, **169**, 162—165).—The authors have measured the dissociation pressures of the sulphones formed by sodium iodide, rubidium iodide, and cæsium iodide respectively (compare this vol., ii, 341) over a temperature range from -22.5° to 20.9° . The three curves practically meet at -23° , and at the higher temperatures spread out, the sulphone of sodium iodide having the highest dissociation pressure, that of rubidium iodide the next, that of cæsium iodide being the lowest. At 760 mm., the dissociation temperatures increase with the molecular weight of the sulphone. Calculations of their heats of formation show that these vary in the inverse order.

W. G.

The Double Magnesium Potassium Chromate Hexahydrate. A. DUFFOUR (*Compt. rend.*, 1919, 169, 73—76).—The hexahydrate of the double magnesium potassium chromate, $K_2Mg(CrO_4)_2 \cdot 6H_2O$, may be obtained if the two chromates are dissolved separately in equimolecular proportions in two and a-half times their weight of warm water, and the solutions are mixed, filtered, and left to evaporate at a temperature not exceeding 15° . After several days, the hexahydrate separates in tabular crystals, which should be removed at once. The crystals may be dried and analysed, but after five or six hours they begin to change slowly into the dihydrate. This dehydration is far more rapid at 120° , but always stops at the dihydrate. The hexahydrate is thus only metastable at even 10° . The crystals are monoclinic [$a:b:c = 0.7521:1.04984; \beta = 103^\circ 54'$]. This chromate shows a close analogy to the corresponding sulphate and selenate, and with its rubidium and caesium analogues forms an eutropic triad. W. G.

Colloidal Cuprous Oxide. Ruoss (*Zeitsch. anal. Chem.*, 1919, 58, 193—194).—One c.c. of Fehling's solution (copper sulphate 3.5 grams, glycerol 15 c.c., and sodium hydroxide 10 grams per 100 c.c.), 0.5 c.c. of 1% dextrose solution, 1.5 c.c. of urine, and 7 c.c. of water are boiled together and then filtered. The filtrate contains bright red. colloidal cuprous oxide. If 1.5 grams of potassium thiocyanate are added to the 100 c.c. of Fehling's solution, a reagent for the estimation of sugar in urine is obtained.

W. P. S.

Adsorption by Colloidal Copper Sulphide. K. SCHERINGA (*Pharm. Weekblad*, 1918, 55, 431—435).—A study of the simultaneous precipitation of zinc with the copper sulphide in the separation of copper and zinc. The amount of zinc carried down decreases rapidly with increase in the concentration of acid present and also with rise in temperature for a given acid concentration. The author concludes that the zinc is not adsorbed superficially by the copper sulphide gel, but that at the moment of precipitation a solid solution of zinc in copper sulphide is formed. W. S. M.

The Chemistry of Burgundy Mixtures. ROBERT LUDWIG MOND and CHRISTIAN HEBERLEIN (*T.*, 1919, 115, 908—922).

Behaviour of Hydrogen towards Iridium. A. GUTBIER, BERTA OTTENSTEIN, and G. L. WEISE (*Ber.*, 1919, 52, [B], 1366—1368).—The experiments were performed in the same manner as with palladium (Gutbier, Gebhardt, and Ottenstein, A., 1913, ii, 608). The occluded hydrogen is readily expelled by a slight rise in temperature, but removal of the last traces can only be effected by strong heating. The quantity of occluded gas is much smaller than with palladium. The absorption of hydrogen by

iridium with decreasing temperature is at a minimum at about 0° , and with rising temperature is at a maximum at about $+20^{\circ}$.

H. W.

Behaviour of Hydrogen towards Platinum. A. GUTBIER and O. MAISCH (*Ber.*, 1919, 52, [B], 1368—1374. Compare preceding abstract).—The occlusion of hydrogen by platinum black and spongy platinum has been investigated. The former is prepared by adding a boiling solution of chloroplatinic acid neutralised with sodium carbonate to a boiling solution of sodium formate, and is purified by washing with hot water; after being dried in a vacuum over phosphoric oxide or concentrated sulphuric acid, it retains about 0.45% of water and 0.55% of oxygen. Platinum black is converted by dilute hydrochloric acid, and frequently by prolonged boiling of suspensions of it in neutral liquids, into a greyish-black modification, which is reconverted into the black variety by treatment with sodium formate in slightly alkaline solution, or, preferably, with hydrazine hydrate solution. The greyish-black modification appears to represent an intermediate stage between platinum black and spongy platinum.

The following are the chief results of the investigation. Platinum black is far more active towards hydrogen than is spongy platinum; with the latter, the absorption of more than one volume of hydrogen was not observed, whilst with the former as much as 160 volumes were absorbed. The behaviour of platinum black with respect to absorption of hydrogen with increasing temperature is the reverse of that of spongy platinum, with which the amount of gas absorbed increases with rise of temperature. Below 0° , the absorptive capacity of both modifications of platinum diminishes. Platinum black absorbs the maximum quantity of hydrogen at 0° . H. W.

Mineralogical Chemistry.

Ferriferous Sands in Italy. U. CATTANEO and L. MADDALENA (*Ann. chim. applicata*, 1919, **11**, 99—108).—Results are given of analyses of ferriferous sands from various parts of the Latium coast, and also of the magnetites separated from such sands. The percentage of Fe_3O_4 in the sand varies from 10.22 to 13.87, and that of TiO_2 from 1.41 to 1.94. The total amount of magnetite present in these sands and others of the Italian coast is calculated to be more than 600,000 tons, 500,000 tons being contained in sand containing more than 5% of magnetite. T. H. P.

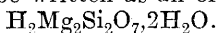
Stalactitic Barytes from Madoc, Ontario. T. L. WALKER (*Amer. Min.*, 1919, **4**, 79—80).—Curious tubular aggregates of minute, white crystals of barytes occur in veins with fluorspar and

calcite. D 4.29. Analysis shows an unusually large amount of strontium. The peculiar form of the mineral is possibly due to deposition on root fibres.

BaO.	SrO.	CaO.	MgO.	Al ₂ O ₃ .	Fe ₂ O ₃ .	SO ₃ .	H ₂ O.	Total.
43.78	13.95	0.98	1.01	1.92	0.48	36.94	0.26	99.32

L. J. S.

Canadian Minerals [Thaumasite, Saponite, etc.]. R. P. D. GRAHAM (*Trans. Roy. Soc. Canada*, 1918, [iii], 12, IV, 191—201).—Thaumasite occurs as a soft, white coating on joint-planes at the contact of nepheline-syenite and crystalline limestone at Montreal. It forms finely fibrous or loose, mealy aggregates of minute needles. Analysis I agrees with the established formula $3\text{CaO}, \text{SiO}_2, \text{SO}_3, \text{CO}_2, 15\text{H}_2\text{O}$; D 1.878. Saponite also occurs at the same locality as a soft, plastic material with much the consistency and appearance of candle grease. On exposure to air, it becomes white and opaque, finally falling to powder, which is soapy to the touch and makes a paste with water. Anal. II, of air-dried material, shows less alumina than is usual in this mineral, and agrees with Clarke's formula, $\text{H}_4(\text{MgOH})_2\text{Si}_2\text{O}_7$. At 40° there is a loss of 8.5%, and since two-thirds of the water is given off below 100°, the formula may be written as an orthodisilicate,



	SiO ₂ .	SO ₃ .	CO ₂	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.
I.	9.38	13.07	6.71	—	—	—
II.	46.45	—	—	3.32	0.42	0.72

	CaO.	MgO.	H ₂ O <100°	H ₂ O >100°.	Total.
I.	27.32	—	—	43.69	100.17
II.	—	25.91	14.48	8.13	99.43

Descriptions are also given of phenakite and of a pseudomorph of bismuthinite after molybdenite from pegmatite and quartz veins in granite at Preissac township, northern Quebec, and of albite with new crystal-forms from Ascot mine, Sherbrooke Co., Quebec.

L. J. S.

Manganotantalite from Amelia, Virginia. O. IVAN LEE and EDGAR T. WHERRY (*Amer. Min.*, 1919, 4, 80—83).—Crystals of "columbite" occurring in albite at this locality are reddish-brown to black in colour, but in thin splinters ruby-red to orange-brown, and the streak is reddish-brown. D 6.50. H 6—6½. Compared with other members of the columbite-tantalite group, it is seen that there is a slight decrease in the *a*-axis with increasing tantalum content:

	Ta ₂ O ₅ . Per cent.	MnO. Per cent.	<i>a</i> : <i>b</i> : <i>c</i> .
Standish, Maine.....	9	4	0.4023 : 1 : 0.3580
Haddam, Conn.....	30	5	0.4020 : 1 : 0.3529
Amelia, Va.	53	8	0.4017 : 1 : 0.3562
Sanarka, Russia	80	14	0.4014 : 1 : 0.3505

L. J. S.

Analytical Chemistry.

Device for Guarding against Over-titration. O. HACKL (*Zeitsch. anal. Chem.*, 1919, **58**, 194—198).—A 25 c.c. pipette having practically no stem below its cylindrical bulb and having a length of rubber tubing on its upper stem is placed in the solution to be titrated. The pipette is filled, the tubing closed with a pinchcock, and the titration proceeded with until the solution is slightly over-titrated; the contents of the pipette are then allowed to flow back into the main portion of the solution, and the titration is continued cautiously until the end-point is reached. W. P. S.

The Estimation of Hydrogen Peroxide and the Conservation of Hydrogen Peroxide Solutions. I. M. KOLTHOFF (*Pharm. Weekblad*, 1919, **56**, 949—959).—Hydrogen peroxide solutions may be conveniently estimated iodometrically. The titration may be carried out directly after the addition of acid and potassium iodide if a few drops of *N*-ammonium molybdate solution are added as a catalyst. For the conservation of peroxide solutions, the addition of 75—100 mg. of acetanilide, benzoic acid, or salicylic acid per litre is recommended. The solution should also react acid to dimethyl-yellow, and should be stored in brown glass bottles.

W. S. M.

The Titration of Iodides by means of Conductivity Measurements. I. M. KOLTHOFF (*Chem. Weekblad*, 1919, **16**, 926—929).—Iodide is completely oxidised to iodine by means of iodate in acid solution according to the equation $5I' + IO_3' + 6H' = 3H_2O + 3I_2$. If the iodide-iodate mixture is titrated with hydrochloric acid and the conductivity measured after each addition of the acid, an approximately constant value is obtained until the oxidation is complete, when a rapid increase in conductivity is observed. The end-point is sharply shown graphically by plotting conductivity against volume of acid added. Iodide may be accurately titrated in this way even in presence of a large excess of bromide, as the analogous oxidation of bromide requires a greater acid concentration and higher temperature.

W. S. M.

Precipitation and Filtration of Barium Sulphate in Water Analysis. VICTOR FROBOESE (*Chem. Zeit.*, 1919, **43**, 367).—The water is rendered slightly acid with hydrochloric acid, boiled, and treated with a very small excess of barium chloride solution; when cold, the liquid is poured through a filter, the precipitate washed by decantation, and then collected on the filter. W. P. S.

Picramic Acid as a Standard in Colorimetric Estimation of Nitrogen by Nessler's Method. G. EGERER and F. FORD (*J. Lab. and Clin. Med.*, 1919, **4**, 439—442; from *Physiol. Abstr.*, 1919, **4**, 167).—The colour of picramic acid solution is practically

permanent, and the solution serves as a trustworthy standard in the estimation of ammonia by Nessler's method. W. P. S.

A Simplified Macro-Kjeldahl Method for Urine. OTTO FOLIN and L. E. WRIGHT (*J. Biol. Chem.*, 1919, **38**, 461—464).—A method by which an estimation of nitrogen in urine may be carried through in twenty to twenty-five minutes. The urine (5 c.c.) is boiled over a micro-burner with 5 c.c. of a mixture of sulphuric and phosphoric acids containing copper sulphate and 2 c.c. of 10% ferric chloride solution. Oxidation should be complete in about eight minutes, whilst the distillation may be carried through in five. Urines containing much sugar require oxidation with fuming sulphuric acid. J. C. D.

Estimation of Ammonia in Blood. SERGIUS MORGULIS and H. M. JAHR (*J. Biol. Chem.*, 1919, **38**, 435—438).—The aeration method for determining ammonia in blood is open to many inaccuracies. The authors propose to remove protein from the blood before carrying out the estimation. This they do by means of metaphosphoric acid. Ammonia in the protein-free filtrate is adsorbed by permutite, from which it is again liberated by sodium hydroxide and determined colorimetrically by the Nessler process. J. C. D.

Method for the Estimation of Nitrates in Water by means of the Phenolsulphonic Acid Reaction. ROBERT C. FREDERICK (*Analyst*, 1919, **44**, 281—284).—The presence of large quantities of chlorides (up to 100 parts of chlorine per 100,000 parts of water) does not interfere with the estimation of nitrates by the phenol-sulphonic acid method if the water (25 c.c.) is evaporated with 2 c.c. of reagent containing 4 grams of phenol and 400 c.c. of sulphuric acid per litre. The evaporation should be carried as far as possible on a water-bath, the residue then dissolved in water, again evaporated, dissolved in 95 c.c. of water, the solution treated with 3 c.c. of concentrated ammonia, diluted to 100 c.c., and the coloration obtained compared with that produced by a known amount of nitrate under similar conditions. W. P. S.

Estimation of Carbon in Soils by the Wet Combustion Method. D. D. WAYNICK (*J. Ind. Eng. Chem.*, 1919, **11**, 634—637).—In estimating carbon in soils and the like by Ames and Gaither's method of wet combustion (*J. Ind. Eng. Chem.*, 1915, **7**, 561), Gortner weighed the carbon dioxide after absorption in potassium hydroxide, whilst Schollenberger (*A.*, 1916, ii, 395) used barium hydroxide as an absorbent and titrated the excess of alkali with acid. The drawback to the first method is the time required for the absorption, and to the second the difficulty of preventing the barium hydroxide absorbing carbon dioxide from the air. These drawbacks are obviated in a simple modification of the method, in which the carbon dioxide is absorbed in a soda-lime absorption bulb and estimated gravimetrically. A

complete estimation may be made in twenty-five minutes. [See also *J. Soc. Chem. Ind.*, 1919, 591A.] C. A. M.

Estimation of Carbon Disulphide. A Critical Examination of the various Methods usually Employed. PERCY E. SPIELMANN and F. BUTLER JONES (*J. Soc. Chem. Ind.*, 1919, 38, 185—187T).—Determination of the specific gravity of benzene before and after extraction of carbon disulphide with alcoholic potassium hydroxide solution gives a fairly accurate measure of the quantity of carbon disulphide present, the error being within 0.03%. Oxidation of the above alkaline extract with bromine and estimation of the resulting sulphate are also trustworthy. Volumetric or gravimetric estimation of the xanthate in the alkaline extract, by titration or precipitation with copper sulphate solution, was found to be untrustworthy, as was also a method depending on the precipitation of carbon disulphide with phenylhydrazine. Precipitation of the xanthate with lead acetate did not yield good results. W. P. S.

Electrolytic Separation of Lead from Chromium and Analysis of Chrome Yellow and Similar Pigments. JAROSLAV MILBAUER and IVAN ŠETLÍK (*J. pr. Chem.*, 1919, [ii], 99, 85—92).—According to Vortmann (*A.*, 1907, ii, 302), the electrolytic separation of lead peroxide in presence of sulphuric, selenic, or chromic acid leads to high results, it being necessary to redissolve the peroxide and repeat the separation. Smith ("Electrochemical Analysis," 3rd ed., 1907, 165), however, states that lead may be separated accurately as peroxide from the alkali and alkaline earth elements, glucinum, magnesium, mercury, and aluminium, and that the presence of chromic acid is without influence on the quantitative separation. The authors find that Pb^{++} may be easily separated electrolytically from Cr^{+++} if 150 c.c. of the electrolytic solution contains 0.2 gram of lead, 0.1 gram of chromium, and 20 c.c. of nitric acid (D 1.4), and that addition of 15 c.c. of perchloric acid (D 1.12) does not invalidate the results. This method is applicable to the analysis of pigments with a basis of lead chromate, the pigment being dissolved in nitric and perchloric acids and the diluted solution electrolysed; the chromium is afterwards precipitated as hydroxide and weighed as Cr_2O_3 . [See also *J. Soc. Chem. Ind.*, 1919, September.] T. H. P.

Estimation of Minute Amounts of Lead in Urine, Fæces, and Tissues. W. DENIS and A. S. MINOT (*J. Biol. Chem.*, 1919, 38, 449—452).—The evaporated urine (2000 c.c.) or the dried tissue or fæces (500 grams) is oxidised with sodium nitrate in a silica vessel. After the oxidation, the vessel is cooled and the contents treated with 10% hydrochloric acid until the reaction is faintly acid. The mixture is heated to boiling, filtered while hot, and made faintly alkaline with ammonium hydroxide. Two or three drops of a 1% solution of copper sulphate are then added, and

the copper and any lead precipitated by the addition of hydrogen or ammonium sulphide. The suspension of sulphides is separated by centrifugalisation, and washed very carefully in order to remove magnesium, phosphates, and chlorides.

The final residue of sulphides is transferred to a platinum crucible of 25 c.c. capacity by means of 3 c.c. of dilute nitric acid (20 parts of concentrated acid, D 1.42, and 80 parts of water), and the centrifuge tube washed out with 3 c.c. of distilled water. The solution is then electrolysed with a current of 3 to 3.5 amperes and 5 to 6 volts, the crucible serving as anode and a spiral of platinum wire as cathode. Within fifteen minutes, all the lead is deposited on the crucible anode in the form of a brown film of lead peroxide, whilst the copper and any traces of iron are deposited on the cathode. Care must be taken not to cut off the current while the lead peroxide is in contact with nitric acid, so that it is necessary to remove the acid by siphon while the electrolysis is proceeding, replacing it at the same time by distilled water. The crucible is washed, and 5 c.c. of a 5% solution of potassium iodide (free from iodate) and 1 c.c. of 25% acetic acid are added. The lead peroxide decomposes, giving a yellow deposit of lead iodide on the crucible and a solution of free iodine. After five minutes, the liquid is transferred to a small beaker and titrated with 0.005*N*-sodium thiosulphate solution.

J. C. D.

Apparatus for Measuring the Volume of Gas Evolved during a Chemical Reaction. P. NICOLARDOT and M. H. ROBERT (*Chim. et Ind.*, 1919, 2, 641—646).—A modification of an apparatus described previously by one of the authors (A., 1912, ii, 597), particularly designed for measuring the volume of hydrogen liberated when aluminium is dissolved in sodium hydroxide solution. The reaction vessel consists of a tube which is connected with a reflux apparatus, and this in turn with the measuring burette. The latter is filled with water and is surrounded by a water-jacket. A diagram of the apparatus is given in the original and the method of using it is explained in detail. W. P. S.

Estimation of Iron in Iron Ores by means of Permanganate. L. BRANDT (*Chem. Zeit.*, 1919, 43, 373—374).—The use of colloidal silica as recommended by Schwarz and Rolfes (this vol., ii, 170) to prevent the action of hydrochloric acid on permanganate in the titration of ferrous salts is untrustworthy. It is shown that the larger the quantity of silica added, the less permanganate is required for the titration. This occurs in both hydrochloric and sulphuric acid solutions.

W. P. S.

Rapid Method for Estimating Nickel and Cobalt in Ores and Alloys. III. W. R. SCHOELLER and A. R. POWELL (*Analyst*, 1919, 44, 275—280. Compare A., 1917, ii, 425).—Further work on the method described previously showed that modification is necessary when the material contains manganese or certain other

elements; the addition of solid potassium iodide instead of saturated sodium chloride solution to the ammoniacal tartrate solution promotes complete precipitation of the cobalt as hexaminecobaltous iodide in the case of ores containing little or no nickel. The following is a summary of the procedure recommended for the analysis of ores.

(1) The ore is free from copper, manganese, calcium, and magnesium; presence of arsenic immaterial. The sample is dissolved in nitric acid, the solution evaporated almost to dryness, and tartaric acid (ten times the weight of trivalent metals present) dissolved in water is added. The mixture is then treated with 50 c.c. of concentrated ammonia and 3 to 5 grams of potassium iodide, and, after fifteen minutes, the precipitate is collected, washed with ammoniacal potassium iodide solution, and dissolved in dilute hydrochloric acid. The solution is filtered, the cobalt precipitated as phosphate, and the nickel titrated in the filtrate from the latter precipitate.

(2) The ore contains copper, otherwise the same as (1). The method is the same as that above up to the point where the iodide precipitate is dissolved in hydrochloric acid. The solution is decolorised by the addition of sulphurous acid, boiled, cooled, filtered to separate cuprous iodide, etc., and the cobalt then precipitated as phosphate.

(3) General procedure for ores free from manganese. The acid solution of the ore is treated with hydrogen sulphide, filtered, the filtrate treated with ammonium chloride and a slight excess of ammonia, and saturated with hydrogen sulphide. The precipitate obtained is dissolved in aqua regia, and the solution is evaporated almost to dryness, etc., as described under (1).

(4) The ore contains manganese. If only small amounts of manganese are present, the ammonium cobalt phosphate precipitate may be titrated with *N*/5-acid (not hydrochloric acid), or the weighed cobalt pyrophosphate precipitate may be dissolved in sulphuric acid and the amount of manganese estimated by the persulphate-silver nitrate method. For large amounts of manganese, the mixed iodide precipitate is dissolved in dilute acid, and the nickel and cobalt precipitated as sulphides from an acetic acid solution, or the acid solution may be neutralised and the cobalt and nickel precipitated as xanthates. In the case of nickel ores free from cobalt, manganese does not interfere with the cyanide titration in the presence of citrate. W. P. S.

Estimation of Urea. PHILIBERT (*J. Pharm. Chim.*, 1919, [vii], 19, 335—346, 386—397, 434—441).—A method which is more trustworthy than those described by Folin and by Fosse (*A.*, 1917, ii, 73), particularly in the case of urine containing sugar, consists in treating 10 c.c. of the urine with 2 c.c. of basic lead acetate solution, diluting the mixture to 50 c.c., and filtering. Ten c.c. of the filtrate are treated with 5 c.c. of 10% sodium hydroxide solution in the ureometer, a definite volume of hypobromite is

added, and the mixture shaken so as to mix it thoroughly with the mercury contained in the apparatus. The gas evolved is measured under the usual conditions. A control experiment is made, using a standard urea solution and the same quantities of reagents as in the first experiment. Allowance is made for any ammonia present, this being estimated separately. W. P. S.

Ureometer with a Reaction Bulb of Variable Capacity. BOYER (*J. Pharm. Chim.*, 1919, [vii], 19, 346—349).—The apparatus consists of a wide tube constricted at its lower end so as to form a graduated tube; the wide tube is divided into two parts, which are connected by a rubber tube which keeps the two ends a short distance apart. Hypobromite solution and water are introduced into the apparatus so as to fill the graduated portion, a glass ball is then placed in the apparatus, thus closing the top of the graduated tube, and the solution in which the urea is to be estimated is added. The two wide tubes are now pressed together, thus folding the rubber connexion in pleats, the whole apparatus is filled with water, closed with a rubber stopper, and inverted. The contents mix, the volume of the gas liberated being accommodated by the rubber connexion; the total volume of the gas is determined in the usual way. W. P. S.

A Reaction for Lecithin. H. J. HAMBURGER (*Arch. Néerland. physiol.*, 1919, 3, 361—364).—This test will detect 0.01% of lecithin present in fluids containing proteins. The proteins are removed by adding three volumes of 96% alcohol and filtering or centrifugalising. On the addition of dilute sulphuric acid (1:5) to the clear filtrate, a cloudy precipitate of lecithin is formed, which dissolves on warming and reappears on cooling. J. C. D.

Detection and Estimation of Cocaine, Heroine, and Veronal in Viscera. P. A. ELLIS RICHARDS (*Analyst*, 1919, 44, 192—196).—A weighed portion of the viscera is acidified with acetic acid and extracted with warm alcohol; the alcoholic solution is concentrated, filtered, clarified with lead acetate, and the excess of lead removed as sulphide, again concentrated, acidified with acetic acid, and extracted with ether. The ethereal extract is evaporated, the residue dried, weighed, and examined for veronal, trional, sulphonal, etc. The aqueous solution, after the extraction with ether, is rendered ammoniacal, extracted with chloroform, the chloroform solution shaken with dilute hydrochloric acid, this acid extract again rendered ammoniacal, extracted with chloroform, and the residue, if any, obtained after evaporating the chloroform, is extracted with benzene, in which cocaine is distinctly soluble. For the examination of the urine, the sample is acidified with acetic acid, boiled, clarified with lead acetate, and then treated as in the case of viscera. The final residues are then submitted to special tests for their identification.

Notes are given on tests for certain narcotics. [See, further, *J. Soc. Chem. Ind.*, 1919, 512A.] W. P. S.

The Metabolism of Bile Acids. I. A Quantitative Method for Analysis of Bile Acids in Dog's Bile. (Miss) M. G. FOSTER and C. W. HOOPER (*J. Biol. Chem.*, 1919, **38**, 355—366).—Dog's bile contains taurocholic and taurocholeic acids, which, on hydrolysis, yield cholic and choleic acids and taurine. Taurine reacts quantitatively with nitrous acid under the conditions employed in the Van Slyke apparatus, and this fact is made the basis for the analytical procedure. Five c.c. of bile cleared in a centrifuge are precipitated with 40 c.c. of 96% alcohol, and heated to boiling point to ensure complete solution of the acids. After cooling, the mixture is made up to 50 c.c. with 95% alcohol and passed through a dry filter. Two portions of 20 c.c. are evaporated to dryness. One is washed out with water and made up to 10 c.c. in a volumetric flask. Samples of 2 c.c. of this are used to determine the nitrogen present in amino-form before hydrolysis. The other sample is hydrolysed by being heated on the water-bath for five hours with 6 c.c. of 8% sodium hydroxide. This sample is made up to 10 c.c. and the amino-nitrogen again determined in 2 c.c. portions. The difference represents the nitrogen present in the amino-group of taurine. For conversion of the nitrogen figure into one representing taurocholic acid, the factor 36.72 is used.

J. C. D.

An Electrical Method of Determining the Lime Requirement of Soils. C. J. LYNDE (*Trans. Roy. Soc. Canada*, 1918, [iii], **12**, III, 21—26).—Two lots of 10 grams each of soil are shaken respectively with 150 c.c. of distilled water and 150 c.c. of a solution of calcium hydrogen carbonate for three hours, as in the Hutchinson and MacLennan method (compare A., 1914, ii, 784). The electrical resistance of the aqueous soil solution and of the calcium hydrogen carbonate solution before and after shaking with the soil is determined. If these are represented by r_1 , r_2 , and OR respectively, then the value of r , the calculated resistance of the calcium hydrogen carbonate solution after being shaken with the soil and allowing for the resistance of the aqueous soil solution, is given by $r = r_1 \times OR / (r_1 - OR)$. Then the ratio r/r_2 should give a measure of the alkalinity or acidity of the soil. Comparing these results with those obtained by the Hutchinson and MacLennan method (*loc. cit.*), it is found that if the ratio is less than 0.986, the soils are alkaline, whilst if the ratio is above 1.284, the soils are acid and require liming.

W. G.

General and Physical Chemistry.

Index of Refraction and Molecular Refraction of Aqueous Solutions of Nicotine. AUGUSTO LEVI (*Atti R. Ist. Veneto Sci.*, 1915, **75**, 465—479).—Measurements were made by the method of minimum deviation on a good spectrometer. The temperature was not constant, but was kept sufficiently near 24°. Sixteen concentrations were used. Pufrich's method of calculation is: $P[(n-1)/d][(1-\alpha C)/(1-C)] = P_1[(n_1-1)/d_1] + P_2[(n_2-1)/d_2]$. P , P_1 , P_2 are the weights, n , n_1 , n_2 the refractive indices, and d , d_1 , d_2 the densities, respectively, of the mixture and of the two components. C is the coefficient of contraction, and equals $(d-d_0)/d$, in which d_0 is the density the mixture would have if no contraction took place on mixing, and α is a constant derived from the empirical relation $(d-d_0)/d = \alpha[(n-1)-(n-1)_0]/(n-1)$, in which $(n-1)_0$ is the value $n-1$ would have if no contraction took place. This gave results more consistent with experimental data, and indicated that methods of calculation based on the hypothesis that the n of mixtures is additive are not accurate. The molecular fraction for water (q_a) and nicotine (q_b) was calculated by the method of Schulze. $q_a + q_b = 1$; $q_a = (p_a/m_a)/[(p_a/m_a) + (1-p_a)/m_b]$; $q_b = (1-p_a/m_b)/[(p_a/m_a) + (1-p_a)/m_b]$; the experimental molecular refraction calculated from the rule of mixtures, according to the Dolezalek-Schulze theory, shows that the water and nicotine form solutions without dissociation phenomena.

CHEMICAL ABSTRACTS.

Optical Activity. I. Temperature-rotation Curves for the Tartrates at Low Temperatures. T. S. PATTERSON and K. L. MOUDGILL (*Proc. Roy. Soc. Edin.*, 1919, **39**, 18—34).—Rotation-temperature curves have been produced from measurements of the rotation of ethyl *d*-tartrate and isobutyl dibenzoyl-*d*-tartrate dissolved in cinnamaldehyde and ethylene dibromide respectively at a series of temperatures from 0—181° in the first-named solvent and 17.7° and 39.7° in the last-named solvent. A consideration of the present results and previously published results (T., 1908, **93**, 1844; 1912, **101**, 378; 1913, **103**, 152; 1916, **109**, 1145) shows that a general temperature-rotation curve may be produced for all tartrates. J. F. S.

Value of the Silver Oun. W. M. HICKS (*Phil. Mag.*, 1919, [vi], **38**, 301—317. Compare A., 1913, ii, 810).—A theoretical paper in which an attempt is made to calculate the value of the ounce for silver to an accuracy of 1 per 100,000. In general, it is shown that $q = 361.7837 + 0.001628dN \pm 0.0038$, for silver $\delta = 421.0470 + 0.001894dN \pm 0.0045$. If the atomic weights in terms of the silver value are determined from the ounce, the values are independent of the actual N used, provided it can be taken as the same for all elements. They should be calculated, therefore, either

with $N=109675$ if in $R.A.$ or 109678.6 if in $I.A.$ and the value $q=361.7837\pm0.0038$ used. J. F. S.

Series Spectra according to the Bohr Atom Model. FRANZ TANK (*Ann. Physik*, 1919, [iv], **59**, 293—331).—A mathematical paper in which relationships of the series spectra are deduced on the basis of Bohr's conception of the atom. These relationships are examined in connexion with the series spectra of hydrogen, helium, parhelium, and lithium. J. F. S.

Principle of Choice and the Displacement Law for Series Spectra. W. KOSSEL and A. SOMMERFELD (*Ber. Deut. physikal. Ges.*, 1919, **21**, 240—259).—A theoretical paper in which the co-ordination of spectrum lines into series on the basis of the quantum theory is discussed. It is shown that the series of doublets of the alkaline earths are spark spectra; their character as a system of doublets explains itself from the doublet character of the arc spectrum of the alkalis. A simple numerical relationship exists between the spark spectrum of the alkaline earths and the arc spectrum of the next preceding alkali metal. J. F. S.

Effect of an Electric Field on the Pressure Displacement and the Broadening of Series Lines. M. RITTER (*Ann. Physik*, 1919, [iv], **59**, 170—184).—The effect of an electric field of approximately 26,000 volt/cm. on the series lines of zinc, mercury, lithium, and calcium is to cause the pressure displacement and the unsymmetrical broadening to increase along a series with increasing member number, and also with decreasing wave-length. The sign of the displacement by an electric field is always the same as the sign of the displacement by increase of pressure and the sign of the dissymmetry. These results confirm experimentally Stark's hypothesis that the pressure displacement and the unsymmetrical broadening is brought about by an intra-molecular electric field. J. F. S.

Structure of the Band Spectra of Burning Hydrocarbons. T. HEURLINGER and E. HULTHÉN (*Zeitsch. wiss. Photochem.*, 1919, **18**, 241—248).—The band spectrum of an acetylene flame has been photographed in the first three orders by means of a concave grating 6.4 m. diameter ruled 400 lines per cm. The bands in general can be represented by three whole numbers, m , n , p , and a second class of bands in which the n , p , values correspond with a system of six series, P_i , Q_i , and R_i ($i=1, 2$). The lines of these six series are given in the paper and the relationships between them worked out. J. F. S.

Effect of an Electric Field on the Spectrum Lines of Argon. TOSHIO TAKAMINE and NOBORU KOKUBU (*Mem. Coll. Sci. Kyoto*, 1919, **3**, 281—285).—The Stark effect on the argon spectrum lines has been examined, using a field of 170,000 volt/cm., by Lo Surdo's method. The lines $\lambda\lambda$ 4933.5, 4510.9, 4335.4, 4333.7, 4300.2, 4272.3, 4259.5, 4200.8, 4198.4, 4191.0, 4182.0, 4164.4, 4158.7, 4153.0, 4132.0, 4046.0 Å. are all slightly displaced toward the red.

Practically all the lines affected by an electric field belong to the red spectrum of argon, and the so-called arc lines seem to be more easily affected than the spark lines. This is in keeping with the results obtained in the case of helium, calcium, and magnesium. The mercury line λ 4339 Å. was found to be displaced about 0.7 Å. for the *p*-component and 0.5 Å. for the *s*-component toward the red end in a field of 53,000 volt/cm.

J. F. S.

Effect of an Electric Field on the Spectrum Lines of Helium. III. TOSHIO TAKAMINE and NOBORU KOKUBU (*Mem. Coll. Sci. Kyoto*, 1919, **3**, 275—280. Compare A., 1918, ii, 253).—The effect of an electric field on the spectrum lines of helium has been continued with the lines $\lambda\lambda$ 4009, 3889, 3868, 3830, 3448, 3188, and 2945 Å.; these lines are examined for the first time. The lines $\lambda\lambda$ 4438, 4121, and 3965 Å., which have previously been stated to be slightly displaced by an electric field, are found to be resolved into a number of components all of which are displaced in the same direction. A striking similarity is noted between the Stark effect on the helium lines $\lambda\lambda$ 4388 and 4026 Å. and the H γ line in the fact that the central line in the *s*-component is the strongest of all the components, and it is displaced toward the red as the field strength is increased. In the present work an echelon grating was used for examining the Stark effect, and the advantages of this arrangement are discussed. The faint line accompanying $\lambda\lambda$ 5876 and 4472 Å. has been examined in this way. Numerous diagrams and photographs are appended to the paper.

J. F. S.

Effect of an Electric Field on the Spectrum Lines of Hydrogen. II. TOSHIO TAKAMINE and NOBORU KOKUBU (*Mem. Coll. Sci. Kyoto*, 1919, **3**, 271—273. Compare A., 1917, ii, 401).—Experiments previously described have been repeated with slight modifications; a tantalum cathode was used instead of an aluminum one, and the pressure in the tube was further reduced, so that it was possible to obtain a field strength of 150,000 volt/cm. It is shown that the central line in the perpendicular component of H γ is shifted about +1 Å. at a field of 130,000 volts/cm. In the case of the H α line six *p*-components and three *s*-components were observed, a fact in keeping with the later work of Stark (*Ann. Phys.*, 1915, **48**, 183). In the secondary hydrogen spectrum the authors have noted a further eleven lines in the region below λ 4000 Å. which are affected by an electric field.

J. F. S.

Spectrum Lines of Oxygen and Nitrogen in an Intense Electric Field. USABURO YOSHIDA (*Mem. Coll. Sci. Kyoto*, 1919, **3**, 287—297).—The Stark effect on the spectrum lines of oxygen and nitrogen has been examined in fields up to 16.5×10^4 volt/cm. and a positive result observed with the lines $\lambda\lambda$ 4100 and 4110 Å. of nitrogen and with some of the lines belonging to the first and second subordinate triplet series of oxygen. Excepting a few ambiguous cases, the amount of displacement or of separation of each of these lines is nearly equal respectively in both the parallel and

perpendicular components. The behaviour of the lines of the second subordinate triplet series of oxygen in the electric field is similar to that of the lines belonging to the second subordinate series of helium and parhelium. The effect on the spectrum lines of the first subordinate triplet series of oxygen is larger than that on the second subordinate triplet series. Each of the lines $\lambda\lambda$ 5329.5 and 4968.5 Å. of the first subordinate triplet series has two isolated components respectively in its immediate violet side. The isolation of the said components becomes smaller as the term number of the series increases. This is exactly similar to that of the isolated components of helium and parhelium. Diagrams and photographs of the resolved lines are appended to the paper.

J. F. S.

Lithium Spectrum in an Electric Field. USABURO YOSHIDA (*Mem. Coll. Sci. Kyoto*, 1918, **3**, 161—171).—The effect of an electric field of 30,000 volt/cm. on the lithium lines $\lambda\lambda$ 6103.8, 4602.4, 4132.4, and 4148.2 has been determined by Lo Surdo's method. The line λ 6103.8 is unaffected by the field employed. In the case of the line λ 4602 two vertical and two parallel components only were observed; the central component observed by Stark did not appear. The separation of the parallel components is somewhat greater than that of the perpendicular components. The intensity of the violet component is less than that of the red component. The line λ 4132 is separated into three components, the displacement of the parallel components being somewhat smaller than those of the perpendicular components. The helium lines have been compared with the lithium lines under the same conditions of treatment. The peculiarity of the lines $\lambda\lambda$ 4602 and 4148.2 in the arc has been explained as due to the effect of an electric field on these lines. Photographs of the separated lines are appended to the paper.

J. F. S.

Effect of an Electric Field on the Spectrum Lines of Calcium and Magnesium. TOSHIO TAKAMINE and NOBORU KOKUBU (*Mem. Coll. Sci. Kyoto*, 1918, **3**, 173—181).—Making use of Lo Surdo's method, the effect of an electric field on the calcium and magnesium lines has been investigated. Quantitative measurements have been made with the calcium lines $\lambda\lambda$ 4685, 4355, 4099, 4095, 4093, 3645, and 3631 Å. and with the magnesium lines $\lambda\lambda$ 4352, 3097, and 3093 Å. The maximum electric field employed was 90,000 volt/cm. The above-mentioned lines and others between $\lambda\lambda$ 5042 and 3624 Å. which were not measured were all displaced in one direction or the other in the electric field. In general, the lines belonging to the same series were affected in nearly the same way, and, further, each line constituting a triplet was affected in the same way. The latter is well shown in the case of the lines $\lambda\lambda$ 4099, 4095, and 4093 Å. belonging to the narrow triplet series. The magnesium triplet $\lambda\lambda$ 3838, 3833, and 3830 Å. seems to be an exceptional case, but as the lines are only very slightly affected, further experiments, using a larger dispersion, are

needed for confirmation. Photographs of the displaced lines are appended to the paper. J. F. S.

The Arc Spectrum of Dysprosium. JOSEF MARIA EDER (*Sitzungsber. K. Akad. Wiss. Wien*, 1918, II A, **127**, 1100—1228; from *Chem. Zentr.*, 1919, i, 914. Compare A., 1918, ii, 181).—It appears possible on spectroscopic evidence that an unknown element, closely related to terbium, is present in the terbium-dysprosium fractions, the spectrum of which is mixed with that of the actual terbium and dysprosium. To obtain further insight into this probability, the author has examined the arc spectrum of pure dysprosium over its whole length. The specimen used was supplied by Auer von Welsbach. The sulphate was converted into the chloride since the latter salts of the rare earths give more powerful arc spectra with less prominence of carbon bands than do the oxides or sulphates. The colour of the arc flame was pale green, but not nearly so intense as with cassiopeium and aldebaranum. The wave-length table given by the author contains 4385 lines, including many new ones in the red, yellow, and extreme ultra-violet regions. No definite evidence of fission of dysprosium is obtained, so that it may be regarded as a well-defined element which can be isolated in the pure condition by various processes of separation, and through the spectrum of which further information may be obtained with respect to the yet uncertain terbium. The lines of the dysprosium arc spectrum are generally sharp, and only broaden slightly after protracted illumination; in addition, a more or less well-defined band spectrum is shown in the visible portion. The first of these bands has its main edge at 5693 Å.U. The second, broadened band has its brightest edge at 5404; the main edge of the third, well-defined band lies at 5263. Contrary to the views of Eberhard, the lines of dysprosium are not generally present in the spectrum of the sun, in which the presence of this element cannot be detected. H. W.

Is the Absorption [of Light] (Vierordt) a Characteristic Value, Independent of the Apparatus (Spectrophotometer) Employed? PAUL HÁRI (*Biochem. Zeitsch.*, 1919, **95**, 266—271).—The values are characteristic, and are not influenced by the type of apparatus, provided the construction and calibration of the instrument are satisfactory. J. C. D.

Absorption Spectra of Aqueous Solutions of Colourless Metallic Complex Salts. YUJI SHIBATA, KURAZO FUKAGAWA, and JUN ASADO (*J. Tokyo Chem. Soc.*, 1919, **40**, 311—338).—The following solutions were used: $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$; $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$; $[\text{Ag}_2(\text{NH}_3)_2]\text{SO}_4$; $[\text{Ag}(\text{NH}_3)_2]\text{NO}_3$; $[\text{Cu}(\text{CS} \begin{smallmatrix} \text{NH}_2 \\ \text{NH}_2 \end{smallmatrix})_3]\text{Cl}$; $[\text{Zn}(\text{NH}_3)_4]\text{Cl}_2$; $[\text{Zn}(\text{NH}_3)_4]\text{I}_2$; $[\text{Zn}(\text{NH}_3)_5]\text{SO}_4$; $\text{Zn}_3\text{AsO}_4 \cdot 2\text{NH}_3 \cdot 3\text{H}_2\text{O}$; $[\text{Zn}(\text{CO} \begin{smallmatrix} \text{NH}_2 \\ \text{NH}_2 \end{smallmatrix})_2]\text{Cl}_2$;

$[\text{Sn}(\text{NH}_3)_2]\text{Cl}_4$; $[\text{Cd}(\text{NH}_3)_2]\text{Cl}_2$; $\left[\text{Cd}\left(\text{CO} < \begin{smallmatrix} \text{NH}_3 \\ \text{NH}_3 \end{smallmatrix} \right)_n\right]\text{Cl}_2$;
 $[\text{Al}(\text{NH}_3)_6]\text{Cl}_3$; $[\text{Fe}(\text{CN})_6]\text{K}_4$; $[\text{Co}(\text{CN})_6]\text{K}_3$; $[\text{Co}(\text{CN})_6]\text{Ag}_3$;
 $\text{CuCN}, 2\text{KCN}, \text{KSCN}, \frac{1}{2}\text{H}_2\text{O}$;
 $3\text{AgCN}, 2\text{KCN}, \text{NaCN}$; AgCN, KCN ; $2\text{Hg}(\text{CN})_2, \text{Mg}(\text{SCN})_2$;
 $2\text{Hg}(\text{CN})_2, \text{Ba}(\text{SCN})_2$; $\text{Hg}(\text{CN})_2, \text{AgNO}_3, 2\text{H}_2\text{O}$;
 $\text{Hg}(\text{CN})_2, \text{K}_2\text{S}_2\text{O}_3, \text{H}_2\text{O}$;
 $2\text{Hg}(\text{CN})_2, 3\text{CuCN}, \text{KCN}, \text{KSCN}$; $2\text{Hg}(\text{CN})_2, \text{KOH}, \text{H}_2\text{O}$;
 $\text{Hg}(\text{CN})_2, \text{KSCN}, 2\text{KCN}, \frac{1}{2}\text{H}_2\text{O}$;
 $3\text{Hg}(\text{CN})_2, [\text{Fe}(\text{CN})_6]\text{K}_4, \text{H}_2\text{O}$; $\text{Hg}(\text{CN})_2, \text{HgO}$. The results are given

in sixteen curves; the logarithms of the thickness of the layers are plotted against wave-lengths at the limits of absorption. Aqueous solutions of colourless metallic complex salts absorb the light more than those of their simple metallic salts, showing that the formation of the complex ions is responsible for the phenomenon. In general, ammonia complexes are more strongly absorbent than cyanogen complexes. The absorbing power of complex silver salts is no greater than that of simple silver salts, probably due to the fact that Ag^+ of the simple salts already exists as a complex form of Ag_2 (compare M. Traube, A., 1886, 661). Cadmium and aluminium complexes are equally as transparent as their corresponding simple salts, as far as the ultra-violet zone is concerned (their plates were sensitive to only $\lambda = 2000$); a hypothesis is given for this peculiarity. All complex salts (except those containing cobalt) give only end absorptions, but not absorption bands; occurrence of the selective absorption depends on the characteristic of metals in the complex. Those complexes containing SCN groups produce selective absorptions, regardless of the kind of metals they contain. In complexes having similar structures, the metals which have greater atomic volumes possess less absorptive power than those having smaller atomic volumes. In complexes containing the same metals, even if their structures may be unknown, it is true that the more components the salt has and the more complex it is, the stronger will be the power of absorption.

CHEMICAL ABSTRACTS.

Ultraviolet Absorption of Pyridine, α -Picoline, β -Picoline, and Piperidine. ERNST HERRMANN (*Zeitsch. wiss. Photochem.*, 1919, 18, 253—278).—The absorption spectra of pyridine, α -picoline, β -picoline, and piperidine have been measured in the region $\lambda\lambda$ 2696—3017 for both vapour and alcoholic solutions. For the vapours of pyridine, α -picoline, and piperidine previous measurements were repeated; in the case of β -picoline the ultra-violet absorption is represented by three broad bands. Series, similar to those observed for benzene derivatives, are evolved. In the α -picoline spectrum a series of similar structure to one of the pyridine series is observed. In the case of piperidine a structure is observed which is similar to that observed for benzene and is characterised by the appearance of series which may be resolved into typical groups. The spectra obtained from capillary layers of the liquids

and from alcoholic solutions (1 gram-mol. in 20, 100, and 500 c.c. of alcohol) are made up of ill-defined bands. J. F. S.

Influence of Different Substances on the Absorption of Light by Thin Tungsten Layers. L. HAMBURGER, G. HOLST, D. LELY, and E. OOSTERHUIS (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 1078—1088).—The present paper describes experiments designed to increase the life of tungsten lamps by removal of the tungsten layer produced on the walls of the lamp as it burns. Two classes of substances come under consideration: (i) gases which form less coloured compounds with the tungsten sublimate, and materials which produce these gases; (ii) substances which decolorise the tungsten layer in some way which is probably not chemical. The first group of substances includes chlorine and substances, such as K_3TiCl_6 , which evolve chlorine on heating. This class of substance is reviewed. Experimental work with the second group of substances is described. The light absorption of the tungsten sublimate is decreased when previous to burning the filament is coated with a layer of sodium chloride, sodium phosphate, potassium cyanide, sodium oxide, sodium fluoride, or calcium fluoride. On passing the current through the lamp these substances sublime and are condensed in a non-crystalline condition on the wall of the lamp, and have the effect of increasing the life of the lamp. The action of these substances is not understood, but a discussion is entered into in the paper on the subject. If the deposit is rendered crystalline by the admission of moist air it loses its efficacy. The life of a lamp using sodium chloride is increased 2.6 times, and of one using calcium fluoride 3.3 times. J. F. S.

A New Photographic Phenomenon. DONALD NEIL McARTHUR and ALFRED WALTER STEWART (*T.*, 1919, **115**, 973—974).

The Secondary Radiation Produced by α -Rays. B. BIANU (*Le Radium*, 1919, **11**, 230—234. Compare A., 1913, ii, 371).—By means of an apparatus described, the existence of an ionising radiation (δ -rays), produced by impact of α -rays on glass and metal surfaces, has been clearly put in evidence and the characteristics of the radiation studied. α -Rays from a polonium surface strike a plate, and the ionisation at various gas pressures produced by secondary radiation from the plate is measured in an ionisation chamber below, the upper surface of which is of wire gauze. The ions produced by the α -rays are prevented from reaching the ionisation chamber by a suitable electric field. The secondary radiation consists of (1) a small part of the α -rays reflected, (2) a secondary radiation of the β -type, of velocity 3×10^9 cm./sec., which corresponds with a generating potential of 2400 volts; (3) an electronic radiation of feeble velocity (δ -rays), completely absorbed by 0.5μ of aluminium, and ionising the air over a very limited range, given by $pa=110$, where p is the pressure and a is the range, both in mm. The number of electrons in (3) is about forty times the number of (2) and about ten times the number of reflected α -particles. It does not differ greatly with the character of the surface

struck by α -rays, whether it be of glass or of various metals. Probably these electrons are all emitted with the same velocity, corresponding with about 20 volts, but suffer partial absorption in a very thin film of the generating surface before escaping, so that their actual velocity varies from that corresponding with from 0 to 20 volts. F. S.

The Question of the Existence of Isotopes with the same Atomic Weight. The End Products of the Thorium Disintegration Series. STEFAN MEYER (*Monatsh.*, 1919, 40, 1—14).

—The radiation from a specimen of lead, separated by Soddy from Ceylon thorite of atomic weight 207.77, has been examined to test the view whether one of the two isotopes of lead of the same atomic weight, produced as the ultimate products by the branching of the disintegration series, undergoes further change with emission of radiation as yet undetected. The α -radiation from the lead was found exactly to correspond in intensity with what is to be expected from the polonium regenerated from radium-*D*, which is necessarily present in this lead, being derived from the small amount of uranium in the original mineral. From a solution of the chloride in water, the polonium was separated by electrolysis on a gold cathode, using a platinum anode, and the range and character of its α -rays were found to be identical with those of a preparation similarly separated from Joachimsthal pitchblende. The discrepancy between the atomic weight of this lead, 207.77, and what it should be, 208.0, if both end-products are stable, must be explained otherwise than by supposing one of the products to be unstable. There must be 26% of common lead present to account for the difference, or Lawson's hypothesis (*Sitzungsber. K. Akad. Wiss. Wien*, 1917, 126, 723) that there may be a gradual replacement of thorium by uranium in thorium minerals in the earth may be the explanation. There is also no evidence as to what becomes of the product, supposed to be unstable, derived from the composition of thorium minerals. It is known not to change into mercury or bismuth, and the existence of any large quantity of an isotope of polonium in thorium minerals is also excluded by the evidence. As regards thallium, Exner and Haschek have found considerable quantities by the spectroscope in Cornish pitchblende, but Hoernes, in a careful analysis of 1 kilogram of thorium-rich, but uranium-poor, monazite could not detect thallium, so that it is probable that its presence in uranium and thorium minerals is accidental, not genetic. A review of the whole of the cases where two isotopes of the same atomic weight are supposed to occur by branching of the series leads to the conclusion that there is no certain instance of this known, and that both the end-products of thorium are stable forms of lead of the same atomic weight, and therefore indistinguishable from one another. F. S.

Is the Electrical Conductivity of the Elements Conditioned by the Presence of Isotopes? F. H. LORING (*Chem. News*, 1919, 119, 62—64. Compare this vol., ii, 313).—When the

isotopic percentages previously given (*loc. cit.*) are plotted against the resistivities of a number of metals, a straight line curve is obtained, which implies that there is a foundation for the theory of whole-number isotopes as applied to ordinary elements. Cadmium constitutes the only exception to this rule, but this may be attributed to the unconfirmed peculiarity in the temperature-resistance curve of this element. The theory of conduction is of interest in connexion with the above-mentioned relationship. Thus, if a small-mass nucleus is so close to a large-mass nucleus that the electronic orbits combine to form a figure of eight, the electrons tending to leave the former to pass round the latter, owing to the greater attraction of the larger mass, then overloading the circuit electrically at any point might give rise to a progressive flow of electrons from atom to atom. On cooling the metal, a point might be reached when further cooling would not improve the contiguity of the orbits, so that perfect conductivity of electricity without any oscillation or vibration of the atoms might take place at a temperature just above absolute zero.

J. F. S.

Behaviour of Non-aqueous Solutions of Salts. A. THIEL (*Zeitsch. Elektrochem.*, 1919, **25**, 214).—Polemical against Beutner (this vol., ii, 263), in which the author maintains that the reasons advanced to explain the electrical conductivity of salts in non-aqueous solvents do not clear up the difficulty, and are not justified on the data put forward.

J. F. S.

Activities of the Ions of Strong Electrolytes. DUNCAN A. MACINNES (*J. Amer. Chem. Soc.*, 1919, **41**, 1086—1092).—A theoretical paper in which it is shown that, since the product of the transport number of the chloride ion and the equivalent conductivity is a constant at a given concentration and temperature for the chlorides of the alkali metals and hydrogen, it may be assumed that the activity of the chloride ion in these solutions is also independent of the nature of the positive univalent ion. On this basis, the activity coefficients of both ions of hydrochloric acid have been calculated for concentrations between 0.001665*N* and 0.100*N*. The potential of the normal hydrogen electrode against the normal calomel electrode has also been calculated, and the value $E = 0.2828$ volt obtained.

J. F. S.

Generation of Electricity by Atomising Liquids. (Ballo-electricity). IV. .C. CHRISTIANSEN (*Ann. Physik*, 1919, [iv], **59**, 95—100. Compare A., 1916, ii, 75).—A continuation of previously published work undertaken with the object of ascertaining whether isomerides produce the same electric effect when projected against an electrode in a finely atomised stream. The experiments show that *d*-tartaric acid, *l*-tartaric acid, *i*-tartaric acid, and racemic acid in *N*/10-solution produce exactly the same effect, which is very small and approximates in value to that of the inorganic acids. When the above-mentioned acids are mixed with

alcohol or 2*N*-sodium chloride, the effect is much greater in each case; in the case of the alcohol mixtures, the value is the same for each acid, but with the sodium chloride mixtures the values vary slightly. Propionic acid produces a much greater effect than either of the monochloro-substitution products. Propionic acid and α -chloropropionic acid produce a positive effect, whilst β -chloropropionic acid produces a negative effect. The β -compound does not change its effect on keeping, but the α -compound has a decreased effect on keeping. β -Hydroxybutyric acid in *N*/2-solution has a much larger effect than α -hydroxybutyric acid. Substitution of bromine has a different effect than substitution of chlorine on the ballo-electric effect of organic substances. This fact is shown by experiments with bromal hydrate, chloral hydrate, monochloroacetic acid, and monobromoacetic acid. J. F. S.

Generation of Electricity by Atomising Liquids (Ballo-electricity). V. C. CHRISTIANSEN (*Ann. Physik*, 1919, [iv], 59, 280—292. Compare preceding abstract).—An instrument (ballo-meter) is described whereby the charge on particles of a liquid atomised in air, the charge on the air, and the amount of electricity which has escaped from the particles which have been in contact may be measured. J. F. S.

The Electrolytic Potential of Copper in the Presence of Various Electrolytes. P. BENVENUTI (*Atti R. Ist. Veneto Sci.*, 1916, 75, 1317—1329).—This work was started with the idea of producing an electrolytic deposit of an alloy of copper and manganese, but this was afterwards given up as impossible, and the measurements of the potential of copper in the presence of various electrolytes were systematically continued on account of the information thus obtained in regard to the greater or less stability of the complexes produced in this way, and because the data obtained could be utilised in further investigations. The method consisted in connecting the copper electrode, and the electrolyte in which it was immersed, with a normal calomel electrode, and in measuring the *E.M.F.* of the resulting cell by Poggendorff's compensation method. Measurements were made at 15°. The salt of copper was the sulphate. The copper electrode was immersed in this solution with varying quantities of other electrolytes. The results show that, by the addition of these other substances, the potential of the copper increases in the electropositive direction in proportion to the formation of complex ions. In proportion to the increased stability of the complex ions formed, the electrolytes studied arranged themselves in the following order: sodium formate, sodium acetate, ammonium tartrate, hydrochloric acid, potassium bromide, sodium thiosulphate, and potassium cyanide. The author believes that a more extensive study of these phenomena will reveal interesting relations between the nature of electrolytes co-existing in one solution and the stability of the complexes which are formed.

CHEMICAL ABSTRACTS

Phenomenon of Electrical Supertension. II. A. SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 1106—1111. Compare this vol., ii, 8, 91).—A theoretical paper in which the conditions of the supertension of hydrogen generated when metals act on water are considered on the basis of the phase rule.

J. F. S.

Electrolytic Reduction of Arsenic and Arsenious Acids to Arsenic Trihydride at Cathodes of Different Metals.

LUDWIG RAMBERG (*Lunds. Univ. Arsskr.*, N.F., Abt. 2, 1918, **14**, No. 21, 1—47; from *Chem. Zentr.*, 1919, i, 905—906).—A historical résumé of the literature is given, and the newer, quantitative methods are critically discussed. The latter are all unsatisfactory. The discrepancies between the data of various authors are due partly to deficient technique and partly to the unexpectedly great influence of the nature of the surface of the cathode. Certain new types of electrolytic apparatus are described which are chiefly notable for the type and location of the diaphragm. The errors due to the diffusion of compounds of arsenic and to the wandering of the arsenate ion to the anode, together with their dependence on the nature of the material of the diaphragm, have been investigated. It is found that the wandering of the ions is a considerably more important factor than is diffusion, and is so important that the quantitative reduction of arsenic acid to arsenic trihydride can only be effected at cathodes at which the process occurs very rapidly. Arsenic trihydride is estimated by absorption in standard iodine solution and estimation of excess of the latter with standard arsenious acid.

Cathodes of the following metals have been used: mercury, zinc, copper, silver, lead, iron, tin, cadmium, nickel, and platinum. The results are given in a series of tables, from which it appears that the nature of the cathodic surface has a great influence on the reduction of arsenic acid to arsenic trihydride. The process generally takes place far more rapidly at spongy than at polished surfaces. The nature of the surface appears to be less important in the case of arsenious acid, and in any case the polished surfaces are not less effective than the spongy ones.

Different series are obtained for arsenic and arsenious acids when the metals are arranged in order of reducing power, but without regard to their superficial condition. In no case does the order exactly coincide with that derived from consideration of over-voltage, although a certain parallelism exists between the latter and the power of reducing arsenious acid.

Rapid and complete reduction of arsenic acid to arsenic trihydride only occurs at mercury cathodes, although certain amalgamated metals give moderately useful results. On the other hand, a mercury cathode is unsuitable for the reduction of considerable amounts of arsenious acid, since the arsenic is not hydrogenated as rapidly as it is formed; a solid phase of arsenic or

arsenic amalgam is thus formed which is only very slowly transformed into arsenic trihydride.

The practical value of the methods is demonstrated by a series of analyses. Estimation of arsenic acid, in amounts containing as much as 50 mg. of arsenic, can be readily effected at mercury cathodes with an error of $\pm 0.1\%$. Cathodes of lead, silver, or tin are most useful in the estimation of arsenious acid. The supposed superiority of lead for this purpose is not confirmed, and polished tin appears to be the best material. The same accuracy as in the estimation of arsenic acid at mercury cathodes cannot, however, be attained; with increasing quantities of arsenic, the losses become greater, and reach as much as 0.25% with 20 mg. of arsenic.

H. W.

Removal of Residual Gases, especially from the Electric Glow Lamp. L. HAMBURGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 1062—1077).—By determination of the changes in gas pressure and by spectroscopic observations, it is shown that with the aid of electric discharges phosphorus vapour can be made to react rapidly with all gases except the inert gases. The action observed in the glow-lamp with phosphorus can also be observed with silicates. At high temperatures, silicates undergo fractional distillation. When tungsten and silicates are in contact at a high temperature, a reaction takes place between them by which an alkali metal is liberated. By means of this, as in the case of phosphorus, the residual gases can be removed from glow-lamps with the aid of electric discharges. The reaction between tungsten and glass makes possible the use of this metal for "leading-in" wires. When rapidly cooled, the vaporised silicate has properties different from those of the normal glass, since it is in a supercooled condition, and this condensate can decrease the blackening of the wall of the lamp produced by the vaporised tungsten. If, instead of coating the filament with a silicate, an aluminate, calcium phosphate, magnesium oxide, or silica is substituted, a similar reaction occurs. In the case of silica, it is to be assumed that a trace of free silicon is formed; only quantities of the order 0.001 mg. of silicon show a detectable activity.

J. F. S.

Specific Heat of Argon and Several Polyatomic Gases.

WILHELM HEUSE (*Ann. Physik*, 1919, [iv], **59**, 86—94).—Making use of the method previously employed (A., 1912, ii, 19; 1913, ii, 183), the author has determined the specific heat of argon, carbon dioxide, nitrous oxide, nitric oxide, methane, acetylene, ethylene, and ethane at temperatures varying from the ordinary temperature to within a few degrees of the condensation point. The following values, among others, have been obtained: argon, c_p 15°, 0.531; -182°, 0.556; carbon dioxide, c_p 20°, 0.846; -75°, 0.768; nitrous oxide, c_p 20°, 0.879; -30°, 0.835; -70°, 0.797; nitric oxide, c_p 15°, 1.012; -45°, 1.001; -55°, 1.014; -80°, 1.024; methane, c_p 15°, 2.22; 5°, 2.20; -30°, 2.13; -55°.

2.11; -80° , 2.11; acetylene, c_p 18° , 1.680; -71° , 1.470; ethylene, c_p 18° , 1.527; -36° , 1.371; -68° , 1.314; -91° , 1.291; ethane, c_p 15° , 1.728; -35° , 1.539; -82° , 1.455. In a large table, the values of the density, specific and molecular heats at constant pressure and constant volume, and the ratio of the specific heats at various temperatures and at zero, are tabulated. J. F. S.

Some Molecular Heats at Very High Temperatures.

H. VON WARTENBERG and G. WITZEL (*Zeitsch. Elektrochem.*, 1919, **25**, 209—212).—The molecular heats of the oxides of magnesium, calcium, and aluminium have been determined by burning a mixture of the metal and its oxide in oxygen in a calorimetric bomb. The temperature at which the measurements are made is that of the melting point of the oxide, and this is obtained by using such a mixture of oxide and metal that the oxide is just not melted. Instead of using the oxide as indicator, a mixture of the metal under investigation and finely divided platinum or iridium may be used in such quantities that the metal is just melted. The results obtained represent the upper limit, and are probably accurate to 10—20%; regarded in this way, they are in agreement with the value extrapolated from the curve of values up to 1600° . The following values have been obtained: magnesium oxide, 11.6 cal. at 2780° ; calcium oxide, 14.8 cal. at 2552° ; and aluminium oxide, 29.1 cal. at 2030° . J. F. S.

The Molecular Heat of Binary Metallic Alloys.

AUGUSTO LEVI (*Atti R. Ist. Veneto Sci.*, 1916, **75**, 627—632).—The principle of Dolezalek-Schulze for calculating the molecular refraction of binary liquid mixtures is applied to the calculation of the molecular heat of bismuth-tin alloys. p_a and p_b are the masses of the constituents in a gram of the mixture, m_a and m_b the molecular weights, and q_a and q_b the molecular fractions of the constituents.

$$q_a = (p_a/m_a) / [(p_a/m_a) + (1-p_a)/m_b],$$

$$q_b = [(1-p_a)/m_b] / [(p_a/m_a) + (1-p_a)/m_b].$$

If $C_{a,b}$ is the specific heat of the mixture, (1) $C_{a,b} = C_a p_a + C_b p_b$, and for the molecular heat of the mixture, (2) $C_{a,b}(m_a p_a + m_b p_b) = C_a m_a q_a + C_b m_b q_b$, in which the first member expresses the molecular heat of the mixture as found by experiment, and the second member the value as calculated by the rule of mixtures. Experiments were carried out by the method of mixtures with alloys of lead and of tin with bismuth. Data indicate clearly the formation of a compound of lead and bismuth when the molecular fraction of lead is 0.44. The eutectic is identical with or close to that mixture which gives maximal molecular heat and produces a compound in the alloy. The curve for mixtures of tin and bismuth is more difficult to interpret and suggests further investigation.

CHEMICAL ABSTRACTS.

Latent Heat and Surface Energy. I.

D. L. HAMMICK (*Phil. Mag.*, 1919, [vi], **38**, 240—245).—The author has deduced an

expression connecting the molecular surface energy with the latent heat. This has the form $\rho V/d = L_1 J/6$, in which ρ is the surface energy in ergs per sq. cm., V is the molecular volume, d the molecular diameter, L_1 the internal latent heat per gram-mol. in cal., and J the mechanical equivalent of heat. This equation has been evaluated for a number of gases (6) and organic liquids (23), and is shown to fit the facts remarkably well. A table of the mean diameter of the molecules of the substances concerned is given containing the value deduced from the diffusion, thermal conductivity, refractive index, and the Avogadro constant b .

J. F. S.

Temperature of Explosion for Endothermic Substances.

RASIK LAL DATTA and NIHAR RANJAN CHATTERJEE (T., 1919, 115, 1006—1010).

Calculation of the Relation between the Vapour Pressure of a Solid and that of a Supercooled Liquid at Various Temperatures.

A. BOUTARIC (*Compt. rend.*, 1919, 169, 432—435).—The formula given is $\log_e p_1/p_2 = U_s/2RT \times 1 - T^2/\theta^2$, where p_1 and p_2 are the vapour pressures of the supercooled liquid and solid respectively at T° (absolute), θ the temperature of transformation, and U_s the diminution of total energy at this temperature. In the case of water and benzene, the observed and calculated values agree with one another, but there is a considerable difference between the values for formic acid.

W. P. S.

Dependence of the Vapour Tension of Benzene-Toluene Mixtures on the Temperature.

ALFRED SCHULZE (*Ann. Physik*, 1919, [iv], 59, 73—85).—Making use of the vapour pressure measurements of Mangolt (*Sitzungsber. K. Akad. Wiss. Wien*, 1893, 102, 1071) for mixtures of benzene and toluene, the author has plotted the vapour pressure as a function of the molecular concentration for the temperatures 20°, 30°, 40°, 50°, and 60°. The partial pressures of both constituents are also calculated and plotted. A consideration of the curves, based on the law of mass action, allows conclusions on the molecular complexity of toluene to be drawn. It is shown that at 20° liquid toluene consists of double molecules to the extent of 50%, at 50° to the extent of 8%, and at 60° it is unimolecular.

J. F. S.

Vapour Pressure and Affinity of Isotopes.

F. A. LINDEMANN (*Phil. Mag.*, 1919, [vi], 38, 173—181. Compare this vol., ii, 209).—Though isotopes in principle must be separable both by fractionation and by chemical means, the amount of separation to be expected depends on the way the chemical constant is calculated, and experiments on the vapour pressure and affinity of isotopes would give valuable information on this point.

F. S.

The Possibility of Separating Isotopes.

S. CHAPMAN (*Phil. Mag.*, 1919, [vi], 38, 182—186).—A method of separating a mixture of gaseous isotopes, depending on thermal diffusion, is sug-

gested, and from the mathematical examination of the problem it is concluded that it should prove practicable. If the mixture is kept in two communicating vessels maintained at different temperatures, in the equilibrium condition there is a slight excess of the heavier gas in the colder vessel. For the case of a mixture of equal volumes of neon of molecular weight 20 and of the hypothetical meta-neon of molecular weight 22, supposing the mixture to be contained in two bulbs at absolute temperatures 80° and 800° , the cold bulb would contain in equilibrium 48.9% of the meta-neon and 51.1% of neon. This difference of 2.2% is reduced to 1.2% when the proportions of the mixture are as 10:1, and assumes the molecules to behave as elastic spheres. The time taken for the equilibrium to be reached ought not to be unduly protracted, and the operation can be repeated as often as desired on the fractions obtained.

F. S.

Free Energy of Dilution of Aqueous Sodium Chloride Solutions. ARTHUR JOHN ALLMAND and WILFRID GUSTAV POLACK (T., 1919, 115, 1020—1039).

Connexion between the Atomic Weights, Densities, and Heats of Reaction of the Elements. II. KARL FEHRLE (*Physikal. Zeitsch.*, 1919, 20, 330—342. Compare A., 1918, ii, 296).—The formula put forward previously (*loc. cit.*) for calculating the heat of formation of compounds from the molecular weight and the density has been used to calculate the heat of formation of the chlorides, bromides, iodides, oxides, and carbonates of a number of elements of groups I—V. The results indicate that the formula gives values which are in moderate agreement with the experimental values.

J. F. S.

Vapour Pressures and Densities of Mixtures of Acetone and Methyl Ethyl Ketone. TUDOR WILLIAMS PRICE (T., 1919, 115, 1116—1126).

Density and Temperature. II. W. HERZ (*Zeitsch. Elektrochem.*, 1919, 25, 215—216. Compare this vol., ii, 268).—The author has calculated the density at the absolute zero (d_0) from the values at the critical temperature ($d_{crit.}$), boiling point (d_b), freezing point (d_m), and at 20° respectively for a number of alcohols (8), esters (13), acids (9), hydrocarbons (13), and halogen-substituted hydrocarbons (4) by means of the formulæ $d_0 = 3.75d_{crit.}$, $d_0 = 1.41d_b$, $d_0 = 1.21d_m$, and $d_0 = d_t(0.77 + 0.64T/T_{crit.})$.

The values obtained by the various methods are in fair agreement with one another. The density at absolute zero decreases with increasing molecular weight in the series of alcohols, acids, esters, and aromatic hydrocarbons, but rises with increase of molecular weight in the series of paraffins and halogenated benzenes.

J. F. S.

Are the Divergencies of the Atomic Weights from Whole Numbers to be Explained by Isotopy? O. STERN and M. VOLMER (*Ann. Physik*, 1919, [iv], **59**, 225—238).—Experiments are described in which hydrogen and oxygen respectively are generated and the gas allowed to diffuse under atmospheric pressure. The density of the gas is determined before and after a portion has diffused. In this way, it is shown that the whole of the gas has the same density, that is, hydrogen and oxygen are not mixtures of isotopes. It is also shown that every theory of the structure of atoms, based on the Prout hypothesis, must be capable of explaining the divergence of the atomic weights from whole numbers by means of energy differences. J. F. S.

Solubility. III. Relative Values of Internal Pressures and their Practical Application. JOEL H. HILDEBRAND (*J. Amer. Chem. Soc.*, 1919, **21**, 1067—1080. Compare A., 1916, ii, 518; 1918, ii, 36).—Various independent methods are discussed for calculating the internal pressures of liquids, and although the values obtained differ considerably, yet they are found to be closely parallel. Tables of the relative values are given in the paper for non-polar substances. Other substances may be tabulated with reference to these substances by knowing their densities, together with either surface tension, boiling point, the constant a of the van der Waals' equation, the coefficient of expansion, or the last together with the compressibility. The use of these values is discussed in connexion with predictions concerning the solubilities of solids, liquids, and gases, the distillation of liquid mixtures, molecular weights and association, deviations from the law of mass action, partition coefficients, and the choice of solvent in recrystallisation. J. F. S.

Adsorption Isotherm at Low Concentrations. A. M. WILLIAMS (*Proc. Roy. Soc. Edin.*, 1919, **39**, 48—55).—A theoretical paper in which it is shown that for very small adsorptions the adsorption law has the form $\alpha = \alpha_0 c$ for both gases and solutions. From this expression, adsorption curves have been produced for solutions and found to agree with the curves obtained by Trouton for acetic acid and charcoal (*Rep. Brit. Assoc.*, 1911, 328) and Schmidt-Walter for water, benzene, and toluene (A., 1914, ii, 542). J. F. S.

Surface Tension and Chemical Interaction. G. N. ANTONOFF (*Phil. Mag.*, 1919, [vi], **38**, 417—419. Compare A., 1918, ii, 437).—A theoretical paper in which it is shown that the results obtained in the previous paper (*loc. cit.*) can be obtained whatever law of molecular action is used as the basis of calculation. The results previously obtained depend on the assumption that molecular action takes place according to an inverse fourth-power law. It is now shown that if an inverse n th power law be assumed, the expressions for surface tension (α) and internal

pressure (P), respectively, would be $\alpha = kp^{(n+1)/3}$ and $P = 2kp^{(n+2)/3}$. Thus the formula connecting both quantities is $P = k\alpha p^{1/3}$, where $k=2$, as in the previous paper. The relationship $\alpha_{12} = \alpha_1 - \alpha_2$ does not depend on the law of molecular attraction, but is a result of a certain chemical interaction between the liquids forming the solutions which enables the heterogeneous system to become stable and prevents both layers from mixing.

J. F. S.

Diffusion of Double Salts. D. MERRILL TORRANCE (*Chem. News*, 1919, 119, 66—67).—From experiments on the rate of diffusion of potassium antimonyl tartrate and potassium sodium tartrate, it is shown that the antimony does not diffuse through with three times the velocity of the potassium, as was expected. The experiments also show that the rate of diffusion through dead or artificial tissue is very different from that through living tissue.

J. F. S.

Velocity of Diffusion. HANS BAUER (*Physikal. Zeitsch.*, 1919, 20, 339—340).—Polemical. A number of remarks to the work of Franks (this vol., ii, 100) on the same subject.

J. F. S.

Reactivity of Powdered Glasses. PAUL NICOLARDOT (*Compt. rend.*, 1919, 169, 335—337).—Account must be taken of the degree of fineness of the powder in testing the resistance of glass to solvent action by boiling the powdered material with water and with dilute hydrochloric acid, otherwise concordant results will not be obtained. Powders of various sorts of glass were prepared in three degrees of fineness by sifting, the ratios of the surfaces being substantially 1:2.84:12.8, and the loss in weight of each after boiling in a platinum vessel for three hours with pure water and with $N/10$ -hydrochloric acid was determined. From the tables given, the following examples may be quoted, the figures being the loss per 1000 of the whole glass and the three powders mentioned above:

Jena glass to water,	0.09, 0.25, 0.75, 2.75.
„ „ $N/10$ -HCl,	0.03, 2.00, 5.25, 40.25.
Thuringian (R) glass to water,	0.03, 0.25, 0.75, 5.25.
„ „ „ $N/10$ -HCl,	0.01, 0.75, 3.75, 12.50.
A French glass to water,	0.11, 1.00, 2.00, 10.00.
„ „ $N/10$ -HCl,	0.02, 0.25, 1.75, 17.00.

It will be seen that, contrary to observations on the whole glass, the powder in nearly all cases is attacked more by hydrochloric acid than by water. Further, whilst water attacks powders of different fineness to practically the same extent per unit of exposed surface, the diluted hydrochloric acid in general attacks the finest powder more vigorously than the others in proportion to its surface area.

G. F. M.

Influence of Neutral Chlorides on Chromium Chloride Solutions. M. E. BALDWIN (*J. Amer. Leather Chem. Assoc.*, 1919, 14, 10—19; from *Chem. Zentr.*, 1919, i, 805—806).—It has

been previously shown (Thomas and Baldwin, *J. Amer. Leather Chem. Assoc.*, 1918, **13**, 192, 248) that the acidity of solutions of chromium sulphate, determined by the electrometric process, is increased by addition of chlorides and is primarily diminished, but subsequently raised by addition of sulphates. The influence of the chlorides of sodium, potassium, ammonium, lithium, and barium on the acidity of solutions of chromium chloride has now been investigated, the experiments being conducted immediately after preparation of the solutions and also after preservation during fifty days. The results show that the hydrogen-ion concentration of chromium chloride solutions is increased by the presence of neutral chlorides, although the total amount of acid hydrogen remains constant. When the salts are arranged in order of increasing effect, the following series is obtained: ($\text{KCl} \cdot \text{NH}_4\text{Cl}$), NaCl , LiCl , BaCl_2 . To determine whether the hydrolysis of chromium chloride plays a part in these results, a similar series of experiments has been conducted with hydrochloric acid solutions of approximately the same hydrogen-ion concentration, when similar effects are observed. It is noticeable that the different salts increase the hydrogen-ion concentration in proportion to their capacity of uniting with a larger number of molecules of water in accordance with the theory of hydrates. Comparison of the results obtained with solutions of chromium chloride and hydrochloric acid show that the phenomenon does not depend on the hydrolysis of the former, since the changes in either case are of the same order and approximately of the same magnitude. On the other hand, the changes which occur after some time in the "actual acidity" of chromium chloride solutions appear to depend on the nature and amount of chromium chloride present. An explanation of the increase in the hydrogen-ion concentration of chromium chloride solutions caused by the addition of neutral chlorides has been advanced by Wilson and Kern (*J. Amer. Leather Chem. Assoc.*, 1917, **12**, 455), who suppose that the amount of water available as solvent is diminished by the combination of the salts and their ions with a portion of the water. H. W.

Isomeric Alloys. G. TAMMANN (*Natur. Ges. Wiss. Göttingen*, 1918, 332—350; from *Chem. Zentr.*, 1919, iii, 89—90).—Normal distribution of atoms cannot occur when two metals separate simultaneously at a temperature at which diffusion is impossible in the mixed crystal; in these circumstances, the arrangement is probably irregular. The crystalline or cryptocrystalline products obtained when two metals separate from a solution have been investigated to some extent, but exact comparison with the series of alloys obtained from the molten metals has not previously been possible, since the properties of the latter were only incompletely known. Binary, crystalline, metallic mixtures can be obtained from galvanic cells formed by placing the two metals in a solution of the less noble, by the electrolysis of a solution of the two metals, by precipitation of the one metal on the

other, and by reduction of the solution of the two metals. Before comparing the properties of these mixtures with those obtained from molten masses, it is desirable to obtain an idea of the capacity for diffusion of a metal deposited on a cathode of a second metal; this power is a characteristic of the nascent atom, and is to be distinguished from the mobility of two kinds of atom in a mixed crystal. If a cell consisting of the two metals immersed in a solution of the less noble metal is short-circuited, cations of the latter are deposited on the more noble metal. If, now, diffusion proceeds at a negligible rate, the original potential of the cell is rapidly regained when the circuit is opened; when diffusion is more rapid, the recovery is gradual. If the potentials are measured by the electrometer, the method gives a very sensitive means of detecting diffusion of the less noble into the nobler metal. Solutions of cadmium and copper sulphates have been electrolysed with the object of obtaining information of the effect of the composition of a mixed electrolyte and of the current density on the composition of the cathodic deposit. By suitable variation of these factors, deposits can be obtained the tensions of which vary between zero and the tension of copper towards cadmium. The Cu-Cd alloys obtained from the molten metals behave quite differently, and therefore cannot be identical with the mixtures prepared electrolytically. The relative affinity of the two metals governs the content of precipitating metal in the precipitated metal. When the two metals can unite with one another, the deposit of the nobler metal from the solution is rich in less noble metal; when, however, a compound is not formed, the noble metal is deposited either free from or admixed with but small amounts of the less noble metal. In certain cases, the composition of the precipitate corresponds with that of one of the compounds obtained from the molten mixtures (for example, Cu_2Cd_3 , CuCd_3 , Cu_3Sn); with other pairs of metals, the composition of the precipitates varies greatly in different preparations (with Cu-Zn, Ag-Zn, Ag-Cd). Even in those cases (Cu-Au, Fe-Pt) in which the two metals form a continuous series of mixed crystals from their molten mixtures, the precipitate is rich in the less noble metal. The precipitates from less noble metals appear to be identical with those obtained by the electrolysis of mixed electrolytes; in each case, the composition depends on that of the electrolytes and on the current density at the place of precipitation. The alloys obtained from molten metals are not identical with those prepared by precipitation from mixed electrolytes; this is shown in detail in the cases of $\text{Cu}_3\text{-Sn}$, Au-Ag , Zn-Cu . H. W.

Alteration in the Chemical Behaviour of Metals and their Mixed Crystals by Mechanical Working. G. TAMMANN (*Nachr. Ges. Wiss. Göttingen*, 1918, 351—361; from *Chem. Zentr.*, 1919, iii, 90—91).—The energy content of a piece of metal is increased by cold working; the methods of estimating this increase are described. Permanent deformation of a piece of metal

causes an increase in its energy which depends on the extent of deformation, the degree of working, and also on the nature and temperature of the metal. The mechanical process leads to a disintegration of the metal which corresponds with an increase in potential energy, whilst the latter is also augmented by processes which can occur within the atom itself. A cold-worked metal is less noble in the hard than in the soft condition. Since those layers which lie on the surface are alone affected, a piece of metal which is superficially hardened, but internally still soft, can behave as less noble than a thoroughly hardened piece. These conclusions have been verified by observations on silver wires which had been worked in different manners. The supposedly exceptional position of bismuth could not be confirmed. The increase in the rate of solution of iron caused by cold-working is probably due to the formation of twin lamellæ in the iron crystals. The action limits of chemical reagents on alloys of gold with copper and silver are altered by mechanical working of the alloys. Rolling and hammering imparts increased chemical activity to Ag-Au alloys, which is noticeable when the gold content is far greater than that which corresponds with the reaction limit in soft alloys. Polishing of the alloys has an effect similar to that of converting them into thin foil. The unexpectedly great displacement of the action limits by mechanical working can only be explained by the assumption of an alteration in the properties of the gold atoms; the latter, in consequence of displacement, are much less firmly retained than formerly, and consequently separate more readily from the lattice after removal of the active atoms. An agent, the action of which surpasses the natural limit, is able to remove the protecting gold atoms from the lattice when their number corresponds with that of the normal reaction limit. H. W.

Atomic Structures of Non-metallic Mixed Crystals.

G. TAMMANN [with K. W. SCHMIDT] (*Nachr. Ges. Wiss. Göttingen*, 1918, 296—318; from *Chem. Zentr.*, 1919, i, 782—784).

—In the absence of abnormal double refraction, the occurrence of definite reaction limits enables the distinction to be made between normal and irregular distribution. The phenomenon has been utilised for the purpose of gaining insight into the arrangement of the molecules in non-metallic mixed crystals. The capacity for diffusion of the two components must also be taken into account, since conclusions, based on the absence of reaction limits, are only valid when the diffusion is negligibly small. Reaction limits similar to those observed with metals occur in mixed crystals of salts when they are prepared from the molten materials and tempered for a sufficient period. The action of water on mixed crystals of sodium and silver chlorides has been investigated, both salts being completely miscible in all proportions in the liquid and crystalline conditions. Crystals with 1—0.75 mol. AgCl scarcely yield any sodium chloride to water; those with 0.75—0.625 mol. AgCl give part of the salt, whilst water removes the sodium

chloride completely from those containing 0.625 mol. AgCl and less. The observations thus closely resemble those made on the extraction of Au-Cu and Au-Ag alloys with boiling nitric acid. An explanation of the behaviour of the salts is based on a conception of the distribution of the silver, sodium, and chlorine atoms in the space lattice. This is determined for sodium chloride by means of the Röntgen spectrum, and since sodium chloride and silver chloride form an unbroken series of mixed crystals, a similar lattice may be assigned to the latter. The normal distribution of the different atoms in the assumed structure is indicated for the molar fractions $5/8$ and $6/8$. Diffusion in mixed crystals shows important quantitative differences from that observed with metals. In the neighbourhood of the melting point, the process occurs much more rapidly in metallic than in non-metallic mixed crystals, and is also more noticeable at temperatures considerably below the melting point. This dictum is not based on quantitative determination of the rate of diffusion, but depends on phenomena (such as the rapidity with which layers of mixed crystals become homogeneous), from which an idea of the rate of diffusion can be obtained. Mixed crystals, the content of which in inactive material is greater than that of the reaction limit at high temperature, deposit a portion of the active material as a result of diffusion, the process occurring more rapidly with increasing temperature. If crystalline powders of two substances, one of which is colourless and the other coloured, are pressed together, an idea of the relative rates of diffusion can be obtained by observation of the change in colour at the originally sharp line of contact. With electrolytes, the conductivity, with similar drop in voltage, is a measure of the mobility of the ions involved in the process. Noticeable electrolytic conductivity is an indication of incipient diffusion. With increasing temperature, the conductivity increases from negligible to very considerable values near the melting point. The great differences in the relative rates of diffusion in metallic and non-metallic mixed crystals are shown by the fact that definite reaction limits are much more rapidly developed by tempering with the former than with the latter. The diffusion of compressed substances has been investigated with the following pairs of compounds: dibenzyl and azobenzene, stilbene and azobenzene, sodium sulphate decahydrate and sodium chromate, potassium perchlorate and potassium permanganate, magnesium sulphate heptahydrate and nickel sulphate heptahydrate, mercuric bromide and mercuric iodide decahydrate. Diffusion of the coloured into the colourless substance is only noticeable with isomorphous crystals, the melting points of which are only slightly higher than the temperature of the experiment; even when this is the case, the process only occurs very slowly. The application of the laws of dilute solution to the solubility and vapour tension isotherms of series of mixed crystals is discussed, but the application of the theory is rendered impossible, since equilibrium between solution and mixed crystal is not attained in any reasonable time when equilibrium is deduced

from the normal arrangement of the crystal lattice. Differences in distribution in the lattice cause mixed crystals of similar composition to form normal and abnormal isomerides, which are differently attacked by solutions. Thus mixed crystals of silver and sodium nitrates were prepared (1) by very slowly cooling a mixture of the molten salts, and (2) by cooling a solution of the two salts in aqueous alcohol. When the two products were treated with a saturated solution of sodium nitrate, considerably greater amounts of silver nitrate were dissolved from the latter than from the former. A second example of isomeric mixed crystals occurs with the chlorides of silver and sodium; they are distinguished by the difference in the rates at which sulphide is formed on them by the action of a solution of sodium chloride containing ammonium sulphide. H. W.

Chemical and Galvanic Properties of Mixed Crystals and their Atomic Structure. G. TAMMANN (*Zeitsch. anorg. Chem.*, 1919, 107, 1—239).—A detailed account is given of the author's previously published researches on the discontinuous properties of mixed crystals, and particularly of simple binary alloys, an explanation of these properties in terms of the space-lattice theory being fully discussed. (Compare A., 1917, ii, 448; 1918, ii, 209, 225, 235, 443, 445, 447.) E. H. R.

Method of Growing Large Crystals from Solution. R. W. MOORE (*J. Amer. Chem. Soc.*, 1919, 41, 1060—1066).—The author has produced perfect crystals of potassium sodium tartrate nearly 10 cm. long by the following method. A saturated solution at 35—40° was made up, removed from the excess of solid, heated to 7—8° above the saturation temperature, and rapidly filtered through paper, care being taken that the temperature did not fall to less than 4—5° above the saturation temperature. Small seed crystals are suspended on threads in a jar and the salt solution poured in. The jar is covered with a glass plate and placed in a water-bath 0.5° above the saturation temperature of the solution. The temperature is allowed to fall to the saturation temperature, and then by means of a sensitive thermo-regulator the rate of cooling is regulated to 0.1° per day until the crystals have become perfect. This usually requires one day. Then the temperature is allowed to fall 0.2° per day until the crystals are 1.8—2.5 cm. long, after which the rate of cooling is increased to 0.5—0.6° per day. When the bath has reached the ordinary temperature the crystals are removed and dried by wiping with a soft cloth. J. F. S.

The Effect of Ions of Sodium Chloride and Calcium Chloride on the Electrical Conductivity of Certain Colloidal Mixtures. NEWTON BALDWIN GREEN (*Plant World*, 1918, 21, 303—317).—Cylinders of colloidal gel, such as gelatin, or mixtures of gelatin, agar, and whole wheat flour, are readily penetrated by the ions of sodium chloride and calcium chloride; the initial rate of penetration is not the same for both salts, but after

several hours the rates become identical. At the beginning sodium chloride diffuses more rapidly than calcium chloride, the ratio of the two rates being approximately 10:8. Because of the greater adsorption of the cation in the case of calcium chloride the diffusion of ions is hindered to some extent. This occurs at the surface of the colloid, and may help to account for Osterhout's observation of the decrease in permeability when calcium salts are used. When one salt is allowed to penetrate the colloid for a time and then a second salt substituted, the rate of penetration of the ions of the latter seems to be unaffected by the presence of the former. A mixed solution of sodium chloride and calcium chloride gives a curve of fall of resistance similar to that of either of the constituents alone. It approaches in value more nearly the curve of the predominant salt. The ions of sodium chloride and calcium chloride do not antagonise one another as regards their penetration into certain colloidal gels, notably gelatin, and mixtures of gelatin, agar, and whole wheat flour. Determinations of electrical resistance were made of solutions of gelatin to which had been added salts in varying concentrations. The purpose of these determinations was to show whether electrical resistance varies directly with the precipitability of the gelatin as determined by Fenn. The electrical resistance of the gelatin was found to vary directly with the precipitability, which is greatest at the isoelectric point. The isoelectric point occurs when the unadsorbed positive and negative ions of the added salts balance one another. It is assumed that balanced solutions owe their effectiveness to the fact that the protoplasm adsorbs from them equal numbers of positive and negative ions, thus bringing the condition to the isoelectric point, at which there is greatest ionisation of the protein, greatest amount of precipitation, and greatest (or normal) permeability.

CHEMICAL ABSTRACTS.

The Influence of Electrolytes on the Electrification and the Rate of Diffusion of Water through Collodion Membranes. JACQUES LOEB (*J. Gen. Physiol.*, 1919, 1, 717—745).—The rate of diffusion of water through a collodion membrane separating the pure solvent from a solution depends on two kinds of forces. First, those of gas pressure which are clearly recognisable in the case of solutions of non-conductors, and secondly, electrical forces which become predominant in the case of low concentrations of solutions of electrolytes. In the diffusion of water through a collodion membrane into a solution of an electrolyte the water molecules are either positively or negatively charged according to the nature of the electrolyte in solution, and these charges are a factor in the rate of diffusion.

Solutions of neutral salts possessing a univalent or bivalent cation influence the rate of diffusion of water through a collodion membrane as if the water particles were charged positively, and were attracted by the anion and repelled by the cation of the electrolyte. The same rule applies to solutions of alkali. Solutions of neutral or acid salts possessing a trivalent or quadrivalent cation

influence the rate of diffusion as if the particles of water were charged negatively, and solutions of acids obey the same rule.

It is experimentally shown that the assumption of a difference in sign of the charge of water molecules (according to the two rules just mentioned) explains all the phenomena that can be observed.

A method is given by which the strength of the attractive electric force of electrolytes on the molecules of water can be roughly estimated and the results of these measurements are in agreement with the two rules. The electric attraction of water molecules by electrolytes increases with an increase in the concentration of the electrolyte, but more rapidly at low concentration than at high concentrations. A tentative explanation for this phenomenon is offered. The rate of diffusion of an electrolyte from a solution to pure solvent through a collodion membrane seems to obey largely the kinetic theory.

J. C. D.

Colloid Chemistry of Congo Rubin. Theory of Indicators and the Theory of the Colour Change of Organic Substances. WOLFGANG OSTWALD (*Koll. Chem. Beihefte*, 1919, **10**, 179—288. Compare this vol., ii, 187).—A long theoretical discussion, together with some experimental data, from which it is shown that in the exceptional case of congo rubin variations in the degree of dispersity play the main part in the variations of colour during neutralisation of an acid solution by alkali. It is not to be expected that among the numerous organic colour substances congo rubin alone shows this peculiarity. Consequently, the author still maintains the correctness of his statement (A., 1912, ii, 439) on the basis of the present and previous results. This statement is reiterated in the form: "In the colour change of organic substances, such as indicators, colloid and, in general, dispersoid chemical processes play an important part and in many the controlling part."

J. F. S.

Quinone-phenolate Theory of Indicators. A Spectrophotometric Method for Measuring the Concentrations of the Quinoidal and Lactoidal Salts and the Equilibrium and Affinity Constants of the Phenolphthaleins and Phenolsulphonphthaleins. R. T. BIRGE and S. F. ACREE (*J. Amer. Chem. Soc.*, 1919, **41**, 1031—1050).—Equations are deduced expressing the relationship between the specific absorption index, the specific colour intensity, and the percentage of intensity of coloured quinone-phenolate salt respectively with the equilibrium and affinity constants of the two acid groups of phenolphthalein and phenolsulphonphthalein indicators. A spectrophotometric method is proposed for measuring the concentration of the monobasic, yellow quinone phenol salt and of the dibasic intensely coloured quinone-phenolate salt in any solution, and the percentage of any indicator transformed into the quinone-phenolate salt in alkaline solution. By the use of the equations developed and the experimental data of Howe and Gibson (*Phys. Rev.*, 1918, **10**, 767) and of the authors it is shown that sulphonphthalein indicators are

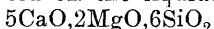
transformed, practically completely, into quinone-phenolate salts, and are therefore very fine, intensely coloured indicators. Phenolphthalein is changed to the extent of only about 44% into the intensely coloured quinone-phenolate salt, the remainder forming the colourless lactoidal and hydrated salts. Tetrachloro-, tetrabromo-, and tetraiodo-phenolphthalein form only about 1—2% of the intensely coloured quinone-phenolate salt, the remaining 98—99% forming the colourless lactoidal or hydrated salts. These indicators are therefore very poor for analytical work. The introduction of 4 atoms of chlorine into the phthalic acid residue of phenolphthalein makes phenoltetrachlorophthalein an excellent indicator, which changes to the extent of 90% into the intensely coloured quinone-phenolate salt. The introduction of halogens into the phenol groups of phenoltetrachlorophenolphthalein gives bromo- and iodo-derivatives, which can only give 17% and 40% respectively of the highly coloured salt in alkaline solution. The spectrophotometric method used in conjunction with the mass action equations gives an approximate measure of the real equilibrium and affinity constants of the two acid groups of indicators of the phenolphthalein and the phenolsulphonphthalein types. The disappearance of the violet band λ 2300 for phenolsulphonphthalein indicates that in alkaline solution the quinone or quinone-phenol group is changed into a quinone-phenolate complex ion like the intensely coloured double compounds made by Jackson (A., 1896, i, 293) by the union of *p*-benzoquinone and phenolates. J. F. S.

Metastable Unmixing and the Classification of Binary Systems. F. E. C. SCHEFFER (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 1055—1056).—A criticism of Buchner's classification of systems in which, in addition to two liquid phases, compounds also occur, and a consideration of the form assumed by the critical line in three phase systems, when unmixing occurs.

J. F. S.

The Ternary System, CaO-MgO-SiO_2 . J. B. FERGUSON and H. E. MERWIN (*Amer. J. Sci.*, 1919, [iv], **48**, 81—123).—Cooling curves have been prepared for the ternary system lime, magnesia and silica; the various products have been examined microscopically. The following substances occur as crystalline primary phases: lime; magnesia; silica (tridymite and cristobalite); pseudowollastonite, $\alpha\text{-CaO, SiO}_2$; 3CaO, 2SiO_2 ; α - and β - 2CaO, SiO_2 ; MgO, SiO_2 (clino-enstatite); forsterite, 2MgO, SiO_2 ; diopside, CaO, MgO, 2SiO_2 ; $5\text{CaO, 2MgO, 6SiO}_2$, and 2CaO, MgO, 2SiO_2 . The melting point of 2CaO, MgO, 2SiO_2 is $1458^\circ \pm 5^\circ$, and the decomposition temperature of $5\text{CaO, 2MgO, 6SiO}_2$ is $1365^\circ \pm 5^\circ$. In addition to these, crystals representing five solid solutions appear as primary phases. These are, (i) a complete series with clino-enstatite and diopside as end members, generally known as pyroxenes; (ii) the pseudowollastonite solid solutions the compositions of which form an area bounded by the following lines: (a) the CaO, SiO_2 - CaO, MgO, 2SiO_2 line; (b) a line running from the composition

CaO, 44.4; MgO, 3.1; SiO₂, 52.5, on the above-mentioned line across to the composition CaO, 46.7; MgO, 3.5; SiO₂, 49.8 on the CaO, SiO₂-2CaO, MgO, 2SiO₂ line; (c) then either the last-mentioned line back to CaO, SiO₂, or, more probably, an approximate continuation of line *b* to about the composition CaO, 50; SiO₂, 50, on the side line. (iii) The wollastonite solid solutions; these extend to about 17% diopside or 3.2% magnesia at the higher temperatures. The most concentrated of these solid solutions along the diopside line (the 17% line) decomposes at $1340^{\circ} \pm 5^{\circ}$, and this solid solution is the only one represented on the liquidus. (iv) The



solid solutions. Only a few of these solid solutions which are decomposed at the temperatures near the decomposition temperature of the pure compound, are stable in contact with a suitable liquid. (v) Certain members of the monticellite solid solutions. Monticellite takes up forsterite in solid solution to the extent of about 10%, and the decomposition temperature of the solution is thereby raised. Monticellite itself probably decomposes at too low a temperature ever to occur as a primary phase. The temperature-concentration relations of the liquids which may be in equilibrium with each of these phases have been thoroughly investigated by means of the quenching method, and the results obtained have been correlated with the existing data on the remainder of the ternary system. The compounds 5CaO, 2MgO, 6SiO₂ and 2CaO, MgO, 2SiO₂ have not been prepared previously. Attempts to prepare a compound of the formula 8CaO, 4MgO, 9SiO₂ (Schaller's åkermanite) gave negative results. The monticellite solid solutions and the compound åkermanite are discussed at length. Experiments were made on the tridymite-cristobalite inversion temperature, which was found, for this system, to be below 1500° ; this is approximately in agreement with Fenner's original value of 1470° . The great sluggishness of the inversion precluded a more exact determination. J. F. S.

Critical Solution Temperature of a Ternary Mixture as a Criterion of Purity of Toluene. KENNEDY JOSEPH PREVITE ORTON and DAVID CHARLES JONES (T., 1919, 115, 1055—1070).

Hydrolysis of some Metallic Acetates. N. LÖFMAN (*Zeitsch. anorg. Chem.*, 1919, 107, 241—264).—For the determination of the degree of hydrolysis of a large number of metallic acetates use has been made of the method of Westerberg (*Arkiv. Kem. Min. Geol.*, 1917, 6). The method consists in shaking a quantity of ether with successive portions of the acetate solution until equilibrium is reached and estimating the acetic acid content of the ether. The distribution-coefficient of acetic acid between water and ether being known, the degree of hydrolysis of the salt can be calculated. Fresh determinations of this coefficient have been made. For dilutions less than $1/15N$ in the aqueous layer it has been found that the distribution-coefficient is independent of the concentration, and for temperatures from 10° to 25° can be expressed by the formula $k = 1.89 + 0.011t$. Double molecules of acetic acid are present in the

ether layer. The presence of acetates increases slightly the value of the coefficient, but not enough to affect appreciably the accuracy of hydrolysis determinations of the acetates.

The degree of hydrolysis of the following acetates has been determined: ammonium, sodium, magnesium, aluminium, chromium, manganese, ferrous, ferric, cobalt, nickel, copper, zinc, silver, cadmium, lanthanum, mercury, and lead. In the case of ammonium acetate the hydrolysis was also determined from measurements of the distribution of ammonia between water and air, and by determining the hydrogen-ion concentration of the acetate solution, the results showing very good agreement among themselves and with the theoretical value. The degree of hydrolysis is independent of the concentration except with ferric and aluminium acetates, the abnormal behaviour of which is attributed to the formation of colloidal hydroxides.

E. H. R.

Quantitative Measurements of the Fission of Hexamethylenetetramine. PAUL TRENDLENBURG (*Biochem. Zeitsch.*, 1919, **95**, 146—163).—The rate of fission of hexamethylenetetramine into formaldehyde and ammonia is greatly increased at high concentrations of hydrogen ion. Thus, it is completely hydrolysed by treatment with 0.1*N*-hydrochloric acid for six hours at 38°. With decreasing hydrogen-ion concentration the rate of decomposition falls, but not proportionally, being slightly slower. In neutral solutions about 1% of the hexamethylenetetramine is hydrolysed on being kept at 38° for six hours. A negative result is only obtained when the solution is distinctly alkaline. From these results it follows that this substance is decomposed to no inconsiderable extent in the stomach. Even slight decomposition probably occurs in the mild alkalinity of the intestinal contents or body fluids. The value of the base as a means of disinfecting the bladder contents depends on the reaction of the urine.

J. C. D.

Active Substance in the Iodination of Phenols. VICTOR COFMAN (T., 1919, **115**, 1040—1049).

Influence of Hydrogen Sulphide on the Occlusion of Hydrogen by Palladium. EDWARD BRADFORD MAXTED (T., 1919, **115**, 1050—1055).

Catalytic Actions at Solid Surfaces. I. Hydrogenation of Unsaturated Fats in the Liquid State in Presence of Nickel. E. F. ARMSTRONG and T. P. HILDITCH (*Proc. Roy. Soc.*, 1919, [A], **96**, 137—146).—Experiments on the rate of hydrogenation of a number of unsaturated fatty oils in presence of finely disseminated nickel have revealed a close analogy between this reaction and the hydrolysis of glucosides in presence of enzymes. The experiments were made with olive oil, cotton-seed oil, whale oil, and linseed oil at about 180°, the rate of hydrogenation being determined by measuring the volume of hydrogen entering and leaving the system by means of water meters. The time-absorption curves,

except in the case of olive oil, are all characterised by an initial linear segment, followed by an abrupt change of direction to a segment of gentler slope, also linear at first but subsequently more or less curved. The position of the point of inflexion of these curves gives the clue to their interpretation. The inflexion takes place on each curve, approximately, at a point when only 10–20% of the glycerides present is derived from acids less saturated than olein. In the case of olive oil this point is reached very soon after the start, and so is difficult to identify on the curve. The curves never approach the logarithmic type required for a unimolecular reaction. The two linear portions represent (1) the hydrogenation of glycerides less saturated than olein, and (2) the hydrogenation of olein itself. Since they are linear they must represent a change in which the acting mass is constant, and, after a reasoned consideration of the possibilities, it is concluded that it is the action of the catalyst that is represented, and, moreover, that the formation of an unstable complex between the nickel and the unsaturated compound must be involved in the reaction.

It has been shown by H. E. Armstrong and others (A., 1913, i, 781) that the hydrolysis of carbamide by urease, and probably most other enzymic reactions, take place at a linear rate, when allowance has been made for the influence of the products of change. The hydrogenation curves show a general resemblance to those obtained in the case of enzymes, and the mechanism of the reaction is probably similar in the two cases, involving the formation and subsequent decomposition of an unstable compound. In each case the interchanges take place in an electrolytic circuit in which the interacting substances and the catalyst or enzyme are all comprised. The action takes place entirely at the surface of minute particles, and the activity of the catalyst depends entirely on the production of the maximum surface and the avoidance of impurities likely to destroy or dirty this surface. E. H. R.

Catalysis. VI. Temperature-coefficients of Heterogeneous Reactions. NILRATAN DHAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 1042–1047. Compare T., 1917, **111**, 707).—A theoretical paper in which it is shown that it is impossible to establish a relation between the order of a reaction and its temperature-coefficient in heterogeneous systems. The temperature-coefficients of catalysed and non-catalysed reactions are also considered. J. F. S.

Neutral Salt Catalysis [Corrections]. HERBERT S. HARNED (*J. Amer. Chem. Soc.*, 1919, **41**, 1092).—A correction of a previous paper under the same title (compare A., 1918, ii, 436). The following corrections are made: p. 1463, the equation $\text{H}_2\text{O}_2 + \text{IO}' = \text{H}_2\text{O} + \text{I}' + \text{O}_2$ instead of $\text{H}_2\text{O}_2 + \text{IO}' = \text{H}_2\text{O} + \text{IO}_2'$; p. 1477, $E_t - E_l$ instead of $E_l + E_t$; p. 1478, in table VII all figures in the column E_l should be positive instead of negative, and the column $E_t + E_l$ should be $E_t - E_l$; and on p. 1479 in table VIII in the column $K \times 10^2/a$, 14.14 should be substituted for 13.14. J. F. S.

Elements in the Order of their Atomic Weight. RAYMOND SZYMANOWITZ (*Chem. News*, 1919, **119**, 58—59. Compare A., 1918, ii, 436).—A further discussion on the atomic weights of the elements based on the condensation theory of their formation.

J. F. S.

The Position of the Electron Orbits in the Atom and the Periodic System of the Elements. P. EHRENFEST (*Chem. Weekblad*, 1919, **16**, 1037—1044).—A lecture delivered before the Nederlandsche Chemische Vereeniging in Maastricht. W. S. M.

Mathematical Investigation of the Stability of A. W. Stewart's Atom. LEONARD C. JACKSON (*Phil. Mag.*, 1919, [vi], **38**, 256—266).—A mathematical paper in which the stability of the atom as conceived by Stewart (A., 1918, ii, 395) is considered. The conditions for the equilibrium and stability of the atom are obtained, and they are applied to several special cases for the helium, lithium, and glucinum atoms. It is found that, in each case tried, equilibrium cannot be maintained indefinitely for the inner ring of negative electrons, even in the entire absence of external perturbing forces. Thus, on the atomic theory considered, instability is placed to the account of those elements which are found to be the least stable in reality. The second alternative put forward by Stewart has not been investigated mathematically, and in view of the fact that the Stewart atom explains physico-chemical facts so well, the author points out that some such alternative suggestion may be reasonably expected to give an atom which is more amenable to ordinary dynamics and more successful in explaining physical phenomena. J. F. S.

Structure of the Atomic Nucleus and its Tendency to Disintegrate. W. KOSSEL (*Physikal. Zeitsch.*, 1919, **20**, 265—269).—A theoretical paper in which the view is advanced that elements of even atomic number up to the value 20 are composed entirely of helium nuclei; beyond this point, the atomic weights indicate the possibility of mixtures. Various cases are considered where α - and β -disintegrations may occur. The author introduces a function z which depends on the atomic weight, and is represented by $z = A/2 - N$, where A is the atomic weight and N the atomic number. The value of z is plotted against the atomic weight, and the curve thus obtained shown to be practically horizontal up to atomic weight 40, and then it rises in practically a linear manner.

J. F. S.

Constitution and Structure of an Atom of Nitrogen. HAWKSWORTH COLLINS (*Chem. News*, 1919, **119**, 29—30).—A theoretical paper in which it is suggested that the nitrogen atom is made up of two hydrogen atoms and one carbon atom. This result is reached from a consideration of the theoretical and experimental

results of Rutherford, J. J. Thomson, and Collie and Patterson, and from a consideration of the relative volumes of the atoms. Thus, the relative volume of an atom of carbon at 15° in all carbon compounds in which the element is united to other elements by single bonds is 0.71. The relative volume of an atom of hydrogen at 15° when united to an atom of carbon in the "first position" is always 15.25. The relative volume of an atom of hydrogen at 15° when united to an atom of carbon in the "fourth position" is always 5.76. The relative volume of an atom of nitrogen at 15° when united by single bonds to other elements is 0.71. The relative volume of an atom of nitrogen at 15° when united to a carbon atom by three valencies is $15.96 = 0.71 + 15.25$. The relative volume of an atom of nitrogen at 15° in nitrates and nitrites is $21.72 = 0.71 + 15.25 + 5.76$. The above results show that the two hydrogen constituents of nitrogen are capable of being expanded from negligible volume to 15.25 and 5.76 respectively.

J. F. S.

Characteristic Ultra-red Frequencies of Diatomic Bohr Gas Molecules and the Specific Heat at High Temperatures.

GERDA LASKI (*Physikal. Zeitsch.*, 1919, **20**, 269—274).—A mathematical paper in which it is shown that, in the sense of Bohr's theory, the molecular model of nitrogen consists of two positive nuclei of charge $7e$ separated 9.1×10^{-9} cm. from each other. Near each nucleus are two rings, an inner ring of very small radius containing two electrons, and an outer, bivalent ring of radius 8.05×10^{-9} cm. containing ten electrons. The plane of the outer ring cuts the molecule symmetrically in two. This molecular model corresponds with an atomic model in which a univalent inner ring of two electrons encircles a nucleus, and concentric with this there is a bivalent outer ring of five electrons. The oxygen molecular model consists of two nuclei of charge $8e$, two inner rings each containing two electrons and an outer bivalent ring of twelve electrons. The oxygen atom model consists of an inner univalent ring of two electrons and a bivalent outer ring of six electrons.

J. F. S.

Distribution of Two Kinds of Atoms in the Regular Frankenheim-Bravais Space Lattices.

G. TAMMANN (*Nachr. Ges. Wiss. Göttingen*, 1918, 190—234; from *Chem. Zentr.*, 1919, i, 781—782).—Experiments on the reaction limits of mixed crystals show that the distribution of two kinds of atoms in a stable complex cannot occur irregularly in accordance with the laws of probability. In the formation of mixed crystals, a distribution occurs with the help of diffusion. After slow cooling of a mixed crystal in which the orderly arrangement of the different atoms has taken place at a higher temperature, a very regular distribution without appreciable variation can permanently persist, as is shown by the fact that the reaction limits are not displaced in the direction of greater concentration of the less active atom

after weeks or months. The crystalline form of well-defined mixed crystals does not differ from that of their components. In similar directions, the properties of mixed crystals are generally as equivalent to one another as in unmixed crystals. Exceptions are found to this rule, however, since in many cases double refraction has been observed in mixed crystals the components of which crystallise in the regular system. The distribution of the atoms is not definitely determined by the postulate of equivalent directions, but becomes definite when the conception of intimate admixture (which occurs at the temperature of rapid diffusion of the atoms) is also introduced. The requirement may be summarised in the statement that accumulations of similar atoms do not occur on the perpendiculars and that the number of lattice perpendiculars of a group is at a minimum. This type of distribution of atom is termed "normal." Two other types of distribution are of interest: (1) such as fulfil the requirements of symmetry but not of most intimate mixture, and (2) those which, whilst having intimate mixture, possess a degree of symmetry lower than that required by the type of lattice. The normal type is the most stable, since, in it, only transitory local changes can be caused by diffusion. Mixed crystals of the third type cannot be optically distinguished from normal crystals into which they should be transformed by rise in temperature. Frankenheim and Bravais have distinguished three types of regular space lattices; the cube, the corners of which are occupied by atoms, is the lattice element of the first, the 8-point lattice. If an atom is considered to be placed in the centre of the cube, the 9-point lattice is obtained, whilst the 14-point lattice is derived by the introduction of atoms at the centres of the faces of the cube in the 8-point lattice. There are two possible ways of determining the normal distribution in these lattices. Either one can choose the corresponding groups in certain directions from the series of groups of lattice perpendiculars, the similar groupings round which are prescribed by the requisite relationships of mixture, or one can dissect the lattices into component lattices. The latter method has marked advantages, but the mixture relationships are thereby definitely fixed. The distribution of the atoms in the various lattices is discussed. The reaction limits of mixed crystals have been studied in such series which have a normal arrangement of atoms. The solubility of hydrogen in palladium, and the limit of this solubility, indicates an instance in which the agent penetrates the lattice; an atomistic explanation of this limit is given on the assumption of a 14-point lattice. In the cases of series of mixed crystals of gold with copper or silver, the reagents do not penetrate the mixed crystals. The atomistic constitution is very closely connected with the different action limits. The differing action limits of different reagents which, for example, withdraw the copper from the mixed crystal, are explained on the assumption that the agents require differing numbers of copper atoms for their action which are only to be found in differing directions. H. W.

Valency Isomerism. J. V. DUBSKY (*Chem. Weekblad*, 1919, **16**, 984—995).—A summary and discussion of some recently investigated cases of valency isomerism. W. S. M.

Physical Nature of Valency. W. KOSSEL (*Naturwiss.*, 1919, **7**, 339—345, 360—366; from *Chem. Zentr.*, 1919, iii, 83—86).—The behaviour of carbon in exhibiting a constant valency, previously considered as particularly simple and typical, must be regarded as exceptional when compared with the majority of elements in which the polar character is marked. In general, a distinction must be made between heteropolar and homopolar linkings. The former not only occur more commonly, but also correspond with the best defined characteristics of valency. The double molecules of elementary gases may be regarded as examples of the latter, and in this connexion the polar neutrality of carbon appears exceptional. The position of carbon among the elements indicates its quadrivalency, but this should be positive from analogy with the preceding elements and negative as judged from its successors. Also, the maximum co-ordination number of carbon and its neighbours is four. A certain stability is thereby caused which is not generally associated with homopolar character, and since similar external conditions are only otherwise associated with silicon (and even then not in the same degree), carbon occupies an almost unique position, which, though rendering it able to form an exceptional number of compounds, makes it quite unsuitable for a general study of valency. The electro-chemical valency theory of Berzelius has been repressed, not only by reason of the preponderating developments of the chemistry of carbon, but also by the apparent necessity of attributing an opposite charge to the two similar portions of a molecule, such as that of hydrogen; this difficulty is removed by the conception of electrons. The electric forces need no longer be regarded as proceeding from the atom as a whole. The individual components exercise attractive force towards one another, and may thus cause the union of atoms without leaving the latter and causing them to be discharged, or certain components, symmetrically arranged, may form a uniting bridge between the atoms. The gradual transition from this type of union to that in which the atoms appear as polar (in which the components have passed from one atom to another and the atom as a whole may be regarded as discharged) is perfectly natural. Bohr's hydrogen model represents the most complete representation of a homopolar molecule. The author gives a historical review of the attempts made since the introduction of the conception of electrons to represent atomic structure and valency with the aid of the quantum theory, and discusses the models of Stark, J. J. Thomson, and Rutherford, together with Bohr's modification of the latter. Since the latter assumes that the electrons of an atom invariably follow their paths in regular order, which is necessary for equilibrium, and since their motion must act externally, as if the charge distributed itself uniformly over the path, the

complete model must appear externally as a symmetrical form, the action of which, after reception or expulsion of electrons, must be governed by the total charge which it has received as a whole. The action of such charges can be calculated with considerable certainty on the assumption that the charges are uniformly distributed, that is, that the resultant charge acts at the centre. A particularly simple electrostatic theory of valency of heteropolar compounds is thus obtained. The process of the union of atoms occurs in two stages, the first consisting in the exchange of electrons, the second in the union of ions. The meaning of the regular course of polar valency activity in the periodic system is discussed. For example, the potassium atom has 19 electrons, which are diminished to 18 when it becomes ionised. With chlorine, on the other hand, the number of electrons is increased from 17 to 18 when the free element becomes ionised. Inactive argon has itself 18 electrons, and this number is also attained by multivalent elements, more distant from argon in the system, in the ionised state. It may be generally stated that the strongly polar elements surrounding the rare gases attain the same number of electrons as the latter when combined. The arrangements of electrons in the rare gases are the most stable, and are the only ones which permit the reception of electrons.

Amongst elements of the type of the rare gases, the common arrangement of electrons occasions repelling forces when the atoms approach one another. On the other hand, alteration in valency is attributed to alteration in the charge of the nucleus, which, in conjunction with the constancy in number of the electrons, imparts a varying total charge to the atoms. The properties of such simple atomic models, having a central charge surrounded by an impenetrable zone, can readily be calculated. Although the atoms, in consequence of integral increase in the total charge, unite in integral ratios, there is nothing in the nature of the model which points to the exercise of special forces in spatially fixed directions, as is indicated by the usual structural formulæ. Actually, atoms frequently exhibit combining powers which cannot be classed with the definite valencies; Werner's complex compounds provide the best known example of this type. A number which represents the degree of charge, and which is identical with the number of chief valencies, is peculiar to each atom of a polar compound. A neutral molecule, for example, must contain equal charges of either sign; two such molecules, however, may yield a third neutral molecule with the help of the attractive forces of their disengaged charges of opposite sign. On the other hand, the degree of charging determines the affinity of one atom for another, and the work necessary to separate them. This work governs the frequency of separation (degree of dissociation of the compound), and the power of a substance to yield ions depends, therefore, on the valency of the atoms. Elements, such as gold, which possess high valency and small volume, are particularly adapted to function as nuclei in complex compounds, and this property is common to all elements

which have one or both of these characteristics. This point of view is further illustrated by reference to the hydrogen compounds of the elements at the negative end of the periodic table. The acidity decreases from fluorine through oxygen to nitrogen in proportion as the hydrogen is more firmly united in consequence of increased nuclear charge. Similarly, in the groups of the periodic system, hydrogen should be progressively less firmly retained as the atomic volume of the second element increases; this is the case in the sixth, but not in the seventh, group. Thirdly, every atom should detach hydrogen ions from electrostatically weaker atoms.

Thus the O of water removes hydrogen ions from compounds of those elements which are placed to the right and below it in the periodic classification. On the other hand, the \bar{N} of NH_3 is more potent than \bar{O} , and therefore removes hydrogen ions from water to form NH^+ and OH^- .

The behaviour of elements exhibiting various degrees of oxidation, or, more exactly, the maximum degree of hydroxylation of such oxides, affords further possibilities of application for the theory. Such compounds can decompose in two ways, yielding either hydroxyl or hydrogen ions. If a definite assumption is made with regard to atomic radius, the work involved in the dissociation of such compounds within the periodic system can be exactly calculated. Highly charged ions are too unstable to be found free in aqueous solution. Electrostatic attractive forces are capable of representing the forces of valency with such exactitude that it appears doubtful whether other forces are involved. A complete representation of the atoms is necessary if the forces in polar molecules are to be exactly ascertained and the dissociation tensions and heats are to be calculated, and, more particularly, if the laws governing homopolar compounds are to be investigated. The experimental methods consist in observations of the natural vibrations of the atoms (Röntgen and optical spectra, etc.), and of the forced vibrations of the electrons of the atoms (refraction and dispersion of light, dispersal of Röntgen rays). The complete representation of the forces which determine the valency action of atoms involves, not only electrostatic, but also electromagnetic, principles, and, in a subsidiary degree, the action quantum.

H. W.

Alignment Chart for the Solution of Molecular Weight and Vapour Density Problems. LESLIE J. HARRIS (*Chem. News*, 1919, 119, 49—51).—A chart, on the principle of the slide rule, is described whereby from weight and volume measurements the vapour density or molecular weight of a gas may be directly read.

J. F. S.

Automatic Extraction Apparatus. JOSEPH TCHERNIAC (*T.*, 1919, 115, 1090—1092).

Inorganic Chemistry.

Manufacture of Metal Chlorides. WILLIAM HEAP and EDGAR NEWBERY (Brit. Pat., 130626).—The anhydrous chlorides of aluminium, magnesium, cerium, and other rare earths are obtained by treating the oxides, or a salt with a weak acid, such as the carbonate or oxalate, with carbonyl chloride at a suitable temperature. With alumina, a temperature of $350\text{--}400^\circ$ is required; magnesia, $500\text{--}600^\circ$; and cerium oxide, 650° . The carbonyl chloride may be replaced by a mixture of carbon monoxide and chlorine, passed over a catalyst, such as animal charcoal, before reaching the metallic oxide, and the process may also be used for dehydrating hydrated chlorides of the above-mentioned metals. Although the patent only applies to the above metals, the reaction is general, and is particularly useful also for the preparation of anhydrous calcium and ferric chlorides. G. F. M.

Preparation of Hydrobromic Acid, using Potassium Bromide, Sulphuric Acid, and Stannous Chloride. ALWYN PICKLES (*Chem. News*, 1919, **119**, 89).—To 25 c.c. of a solution of potassium bromide (90 grams of the salt in 150 c.c. of solution) were added 0.2 gram of stannous chloride and 3.4 c.c. of concentrated sulphuric acid; by distillation at $120\text{--}127^\circ$, a solution of hydrogen bromide was obtained which was free from tin and almost free from hydrogen chloride, the yield being 95%. If a larger quantity of stannous chloride is used, the distillate contains tin and hydrogen chloride. C. S.

Compounds of Arsenious Acid with Iodides of Multi-valent Metals. R. F. WEINLAND and PAUL GRUHL (*Arch. Pharm.*, 1917, **255**, 467—481).—The iodides of a number of bivalent light and heavy metals, as well as that of aluminium, form compounds with arsenious acid. When the moderately concentrated solution of the iodide, saturated in the hot with arsenious acid, is allowed to cool, the compound, sometimes together with a little free arsenious acid, separates in small crystals, which have no distinct crystalline form, or consist of well-formed, microscopic, hexagonal leaflets. The following compounds have been thus prepared:

$\text{GII}_2, 3\text{As}_2\text{O}_3, 8\text{H}_2\text{O}$, $\text{Mg}(\text{or Ca or Sr})\text{I}_2, 3\text{As}_2\text{O}_3, 12\text{H}_2\text{O}$,

$\text{BaI}_2, 3\text{As}_2\text{O}_3, 9\text{H}_2\text{O}$,

$\text{ZnI}_2, 3\text{As}_2\text{O}_3, 10\text{H}_2\text{O}$, $\text{Mn}(\text{or Fe or Co})\text{I}_2, 4\text{As}_2\text{O}_3, 12\text{H}_2\text{O}$,

$\text{NiI}_2, 4\text{As}_2\text{O}_3, 10\text{H}_2\text{O}$,

$\text{AlI}_3, 6\text{As}_2\text{O}_3, 18(?)\text{H}_2\text{O}$, and $\text{LiI}, 2\text{As}_2\text{O}_3, 3\text{H}_2\text{O}$. In general, the characters of the iodides are suppressed in these compounds, which resemble more the arsenites of the metals. In dry air they are moderately stable, but gradually become yellow or brown, with conversion of the arsenious to arsenic acid in the case of the alkaline earth compounds and oxidation of the metal with

the ferrous and manganous compounds; this decomposition is most rapid with the ferrous, manganous, and aluminium compounds, and may be accelerated by heating the compounds in the air. In a vacuum over sulphuric acid or in a current of hydrogen at 100° , the water of crystallisation is completely lost with only minimal decomposition of the compounds; part of the water is reabsorbed from the air. The cobalt salt is pale red, the nickel salt pale green, and the rest colourless. With the exception of that of magnesium, these compounds are sparingly soluble in water, and when heated with water they appear to undergo partial dissociation into the iodides and arsenious acid. When the solutions are evaporated, salts richer in arsenious acid, but of no simple formula, separate out, owing to the fact that the iodide is not in excess as it is in the solutions from which the compounds are originally deposited.

The constitution of the compounds is discussed, and the conclusion is drawn that the anion is formed by union of the molecules of arsenious anhydride with the iodine atom or atoms, whilst the metal forms the cation.

Solutions of chromic and stannous hydroxides in hydriodic acid take up arsenious anhydride, but complete decomposition occurs on evaporation.

Compounds of antimony trioxide similar to the above were unobtainable in aqueous solution, but this oxide dissolves in fused potassium iodide, giving the amber-yellow, transparent, crystalline compound, $8\text{Sb}_2\text{O}_3 \cdot \text{K}_2\text{O} \cdot 2\text{KI}$.

Arsenic trisulphide is insoluble in potassium iodide solution, even on boiling, and solutions of thioarsenites in potassium iodide solution fail to give arsenic trisulphide compounds analogous to those of arsenious anhydride.

T. H. P.

Freezing of Silicic Acid Coagula and the Problem of the Hydrates of Silica. I. and II. B. L. VANZETTI (*Atti R. Ist. Veneto Sci.*, 1915—1916, **75**, 261—266; 1916—1917, **76**, 287—292).—The author describes results of experiments following up the work of G. Bruni (*Rend. soc. chim. Rom.*, 1905, **3**, 2) on the comparison of the dehydration of silicic acid gels by evaporation and freezing. It is found that with gels varying in initial concentration from 3 to 10% of silica frozen at about -20° , the final ratio of water to silica depends principally on the initial concentration being higher the more water was initially present. Substantially the same conditions were reached for dehydration by freezing at -17° as for drying in air at constant temperature and humidity. A marked influence in the age of the gels was observed, similar to that noted by van Bemmelen, in that with older gels freezing produced a much more advanced dehydration. The results are regarded as in agreement with the absorption theory and as giving no support to the view that specific hydrates of silica are concerned.

In the second paper further experiments are detailed in which

both the time of drying was greatly prolonged at normal temperature (15°) and the degree of cooling greatly increased for the freezing experiments, mixtures of carbon dioxide and acetone, and liquid air being used. The results confirm the previous ones for shorter periods and higher temperatures. As before, it was found that the final composition depends entirely on the initial concentration and the age of the gel, and not at all on the temperature of freezing. This independence of the gel state of temperatures down to -200° is regarded as contributing a new datum to the granular theory of the gel constitution. Whilst the status of the last traces of water not removed by freezing cannot yet be decided, the results illustrate the relationship of silicon and carbon and their relative positions in Mendeléev's system; in both cases, in the process of evaporation of water, there is manifest a tendency to the separation of the anhydride passing to conditions of maximal stability, in the one case as solid, in the other as gas.

CHEMICAL ABSTRACTS.

Selective Combustion of Carbon Monoxide in Hydrogen. ERIC KEIGHTLEY RIDEAL (T., 1919, 115, 993—1006).

Sodium Hypochlorite. MALCOLM PERCIVAL APPLEBEY (T., 1919, 115, 1106—1109).

Action of Copper on Sodium Nitrite. WALTER PETERS (*Zeitsch. anorg. Chem.*, 1919, 107, 313—316).—Experiments are described in which metallic copper was warmed at 60° with a 5% aqueous solution of sodium nitrite, in presence of carbon dioxide, air being excluded from the reaction vessel. Decomposition of the nitrite occurred with evolution of nitrous gases. Analysis of the gas and of the residual solution showed that the former contained nitrous and nitric oxides whilst the latter contained nitrate. The decomposition of the nitrite is not catalytic, but chemical, involving simultaneous oxidation and reduction. It has not been found possible to represent the reaction by an equation. Other metals, such as lead, iron (filings), and cobalt dissolve in the nitrite solution, but without evolution of gas. In the case of cobalt, sodium cobaltinitrite is formed in solution. E. H. R.

Manufacture of Strontium Peroxide. JAMES BUCHANAN PIERCE, jun. (Brit. Pat., 130840).—Strontium oxide combines directly with oxygen under a pressure of 105—126 kilos. per sq. cm. at a temperature of 400 — 500° . The resulting peroxide contains over 85% of SrO_2 , and resembles barium peroxide in physical properties. G. F. M.

Anhydrous Phosphates, Arsenates, and Vanadates of Lead. M. AMADORI (*Atti R. Ist. Veneto Sci.*, 1916—1917, 76, 419—433).—Thermal studies of the systems $\text{PbO-P}_2\text{O}_5$, $\text{PbO-As}_2\text{O}_5$, and $\text{PbO-V}_2\text{O}_5$ are described. The investigation was suggested by the analogy of these compounds to the calcium derivatives as in Thomas slag, and in the work of Kroll. Formation of compounds with lead

oxide occurs in the diminishing order P_2O_5 , As_2O_5 , and V_2O_5 . The PbO content is upwards of 66.66% mol. The phosphates, arsenates, and vanadates are pyro- (as $P_2O_5, 2PbO$), ortho- (as $P_2O_5, 3PbO$), and octa- (as $P_2O_5, 8PbO$). In addition, there is an anorthophosphate, $2P_2O_5, 5PbO$, and a metaphosphate, P_2O_5, PbO . A tetraarsenate, $As_2O_5, 4PbO$, is probably also formed.

CHEMICAL ABSTRACTS.

Thallium-Tin Alloys. PAUL FUCHS (*Zeitsch. anorg. Chem.*, 1919, 107, 308—312).—A thermal investigation of the alloys of thallium and tin has shown the existence of a eutectic point at 166° with 30 at. per cent. of thallium. The eutectic horizontal extends from 0 to 73 at. per cent. of thallium; with a greater proportion of thallium the alloy forms homogeneous, mixed crystals. Alloys with less than 73% of thallium show on cooling, in addition to the arrest point at the eutectic temperature, a second arrest at 144.5° . This arrest point represents the transition point of thallium, lowered through the influence of the tin from about 231° , the transition point of pure thallium. In the mixed crystal region, that is, from 73 to 100% of thallium, the transition point is lowered approximately in proportion to the amount of tin present. The arrest point at 144.5° is the transition point of saturated mixed crystals containing 73 at. per cent. of thallium. E. H. R.

Aluminium and a Double Salt. E. RATTENBURY HODGES (*Chem. News*, 1919, 119, 64).—When aluminium foil is submitted to the action of dilute nitric acid for seven to eight weeks it dissolves, and on evaporating the solution a light grey, colloidal mass containing some free acid is obtained. This solid is nearly all hydroxide, and on exposure to a moist atmosphere is completely converted into hydroxide. J. F. S.

Ternary Alloys of Aluminium with Magnesium and Copper. RUDOLF VOGEL (*Zeitsch. anorg. Chem.*, 1919, 107, 265—307).—A thermal and microscopical study has been made of ternary aluminium-magnesium-copper alloys containing up to 55% of magnesium and 54% of copper, and from the results the solid, triangular equilibrium diagram limited by the phases Al , Al_2Cu , and Al_3Mg_4 has been constructed. It is known that, with copper, aluminium forms mixed crystals containing up to 4% of copper, whilst with a greater proportion of copper an eutectic of these mixed crystals and the compound Al_2Cu is formed. It is now found that aluminium also forms mixed crystals with magnesium with a maximum magnesium content of 6%. With more than this proportion of magnesium a second mixed crystal constituent appears containing the compound Al_3Mg_4 . This constituent being hard and brittle, the presence of more than 6% of magnesium in these alloys is likely to be disadvantageous.

The compositions of the ternary alloys examined were so chosen that seven sections of the Al - Al_2Cu - Al_3Mg_4 diagram could be constructed, and from them the complete three dimensional diagram

deduced. These sections and the complete diagram are fully discussed. The following constituents occur in the ternary alloys: ternary mixed crystals of the three elements, ternary mixed crystals containing Al_2Cu , a ternary compound, $\text{Al}_8\text{Mg}_4\text{Cu}$, and binary Al-Mg mixed crystals. When a polished section of a ternary alloy is etched with concentrated nitric acid, the mixed crystals containing Al_2Cu are blackened in about half a minute, the crystals of the ternary compound become brown to black much more slowly, the mixed crystals of the series containing more than 6% of magnesium become yellow, whilst the ternary mixed crystals rich in aluminium remain bright. On adding a drop of water to the nitric acid the black Al_2Cu mixed crystals become bright red owing to the deposition of copper, whilst the ternary compound rapidly blackens. A number of photomicrographs of different alloys are reproduced. The ternary compound forms crystals which are hard and brittle; consequently, it is an undesirable constituent.

Binary alloys of aluminium with 1–10% of magnesium show a secondary arrest point at 584° , with 2–5% of copper at 513 – 529° , and with both magnesium and copper present, between 557° and 564° . It appears probable that this thermal effect is due to an allotropic change of the aluminium induced or accelerated by the foreign constituent. The aluminium used contained some iron and silicon, but no microscopic evidence of the formation of an eutectic with either of these elements could be detected. A similar arrest point was observed by Gwyer (A., 1908, ii, 284) with aluminium alloys containing nickel and cobalt. The possibility of allotropic change of the aluminium does not explain, however, the increase in tensile strength which aluminium alloys containing magnesium and copper undergo after heating to about 500° and cooling to the ordinary temperature. This phenomenon cannot yet be explained.

E. H. R.

Regularities in the Chemical Action of Gases on Iron and its Compounds with Non-metals at High Temperatures.

FRIEDRICH SCHMITZ (*Stahl u. Eisen*, 1919, **39**, 373–381, 406–413; from *Chem. Zentr.*, 1919, iii, 6–7).—When pure hydrogen is passed over strongly heated technical iron or is blown through molten iron (pig iron, ferrous alloys, steel), the non-metals which are present in the free or combined state are converted into the corresponding gaseous hydrides; the behaviour of pure non-metals (carbon, silicon, arsenic) is similar. The hydrides dissociate to some extent at the high temperature, and the nascent hydrogen, in the absence of oxygen, can reduce silica, even at 700° , to silicon hydride. The salts of iron are converted at elevated temperature in the presence of hydrogen into iron and free acids. If, on the other hand, iron is ignited in a gaseous hydride, hydrogen is liberated, which, in part, diffuses into the iron, and the non-metal or acid radicle combines with the iron. Under definite external conditions of temperature and pressure, an equilibrium is set up for each non-metal; a definite relationship between hydrogen and non-metallic hydride is established, at which neither cementation nor

tempering occurs. In an atmosphere of pure hydrogen or nitrogen at an elevated temperature, both carbon and silicon can diffuse into solid iron without previous formation of gaseous substances.

Compounds of iron, oxygen, and the corresponding non-metal are formed when metalloids compounds of iron are ignited in pure oxygen. If these compounds contain carbon, sulphur, or arsenic, they decompose at a higher temperature, yielding ferric or ferrous oxide and the gaseous oxide of the metalloid. If iron is ignited in a gaseous compound of a metalloid, which can be replaced by hydrogen, and oxygen, a compound of iron, oxygen, and the non-metal or hydrogen is first produced. Such compounds, which contain phosphorus and silicon, are stable when the temperature is raised; those, however, in which carbon, sulphur, arsenic, and hydrogen are present decompose at a slightly increased temperature, giving ferric or ferrous oxide and gaseous compounds of the non-metal or hydrogen with oxygen. Nitrogen has no action on non-metals present in solid or liquid iron. The diminution in the carbon content, frequently observed after ignition in nitrogen, becomes progressively smaller as greater care is taken to free the nitrogen from oxygen and gases containing oxygen. H. W.

Alloys of Iron and Nickel Deposited Electrolytically.

P. BENVENUTI (*Atti R. Ist. Veneto Sci.*, 1916, **76**, 453—477).—The author reviews the work of Bruni and Amadori and other experimenters in depositing alloys containing nickel and iron, and describes his own investigations to discover the best conditions for producing the deposit. The composition of the bath and its relation to the composition of the alloy deposited is discussed from his data. The physical structure of Ni-Fe alloys of different composition is shown in photomicrographs. Tables show the atomic % of iron varying from 2 to 97, the duration of the electrolysis, the weight of the alloy deposited, and the weight and % of the iron contained in the deposit. Iron in the alloy was estimated volumetrically by permanganate. The cell was maintained at 25° ($\pm 0.1^\circ$) in a thermostat and platinum electrodes were used. Each electrolysis lasted about eight hours. Current was maintained at 25 milliamp. and the current density at the cathode was 0.5 ampere per sq. dm. The two metals may be easily deposited simultaneously. An ammonium tartrate bath with less than 73% or more than 75% of iron gives deposits containing more and less iron respectively than is contained in the solutions. A bath containing 26% of nickel and 74% of iron deposits an alloy of the same composition, which is that of stable equilibrium at ordinary temperature and pressure, and is also that of the eutectic alloy, and that of the solid saturated solution, the meteoric mineral t  nite, solid solution of iron in nickel, and of kamazite, solid solution of nickel in iron. The deposits by the current are such as to indicate in the deposits the co-existence of two types of saturated solid solution. The study of the electrolytic potential supports the hypothesis proposed above. The micrographic study of the deposits furnishes evidence of the presence of two structures in all the alloys, what-

ever may be their composition. It is probable that in the course of their deposition, the alloys Fe-Ni electrolytically tend, without reuniting, towards the state of equilibrium of nickeliferous iron in the original meteorites.

CHEMICAL ABSTRACTS.

Meteoric Nickel-Iron and the Polymorphism of Carbon-Iron. G. TAMMANN (*Nachr. Ges. Wiss. Göttingen*, 1918, 258—266; from *Chem. Zentr.*, 1919, i, 806—807).—According to Osmond and Cortaud (A., 1904, ii, 135), tænite is to be regarded as a particular phase, since it is sharply separated from kamacite, particularly after being etched. The author, however, is more inclined to regard it as a deposit in kamacite rather than to consider that the substances represent two phases in equilibrium with one another. According to the recent experiences on the reaction limits of chemical agents on mixed crystals, two portions of a conglomerate which show widely differing behaviour towards reagents are not necessarily to be regarded as distinct phases. The determination of limits of action in technical nickel-iron is rendered impossible by the presence of oxygen. It appears questionable whether tænite itself is homogeneous. If the latter is not regarded as a separate phase, there is no difficulty in interpreting the meteoric structure on the basis of the known equilibrium diagrams of nickel steels, and the meteoric structure may be assumed to be due to the crystallisation of the respective molten masses. In this case there must not be expected the normal, stable distribution of the nickel and iron atoms, such as occurs in the space lattice of technically homogenised nickel irons, but a different, unstable arrangement. The structure of meteoric iron shows the manner in which the distribution of both kinds of atoms in kamacite differs from the normal. The atoms of the meteorite, like those of technical nickel-iron, probably occupy the points of a 14-point space lattice, the element of which is the cube with atoms at the corners and in the middle of the sides; the latter occupy the corners of an inscribed octahedron. The difference between kamacite and technical nickel-iron may be explained by assuming that, in the former, the lattice perpendiculars parallel to the edges of the octahedron are occupied by an abnormal number of nickel atoms. It is admitted that a form which is unstable when heated may be permanent when it has separated from the molten state. According to the author, therefore, kamacite is a mixed crystal in which the distribution of the nickel and iron atoms is not normal, but of lower symmetry, similar to the mixed crystals with double refraction. The tænite leaflets are layers orientated on the octahedral planes, whilst plessite represents portions richer in layers. Unstable forms, which are probably to be regarded as space lattice isomerides, are also found in carbon steels.

H. W.

Monoclinic Double Selenates of the Cobalt Group. A. E. H. TUTTON (*Proc. Roy. Soc.*, 1919, [A], 96, 156—184).—Continuing the crystallographic investigation of the salts

of the series $R_2M(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$, the author now reports the results of the examination of the four salts in which M is cobalt and R is potassium, rubidium, caesium, and ammonium. As in the case of the corresponding double ferrous selenates (this vol., ii, 346), all four salts crystallise in the holohedral class of the monoclinic system and are isomorphous with the other members of the series. The relations between the four salts correspond exactly with those found in the case of the salts of the ferrous group.

Potassium cobalt selenate, $\text{K}_2\text{Co}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$, $a:b:c=0.7522:1.0:5062$, $\beta=104^\circ 17'$, $D_4^{20} 2.530$, M.V. 208.6.

Rubidium cobalt selenate, $\text{Rb}_2\text{Co}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$, $a:b:c=0.7427:1.0:5019$, $\beta=105^\circ 14'$, $D_4^{20} 2.837$, M.V. 218.49.

Caesium cobalt selenate, $\text{Cs}_2\text{Co}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$, $a:b:c=0.7310:1.0:4989$, $\beta=106^\circ 18'$, $D_4^{20} 3.094$, M.V. 230.73.

Ammonium cobalt selenate, $(\text{NH}_4)_2\text{Co}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$, $a:b:c=0.7449:1.0:5031$, $\beta=106^\circ 23'$, $D_4^{20} 2.228$, M.V. 218.1.

Comparing the molecular volumes of analogous double sulphates and selenates of the different groups which have been investigated, it is seen that the replacement of one atom of sulphur by one of selenium increases the molecular volume by a quantity varying only between the limits 6.0 to 6.8 units. In the simple alkali sulphates and selenates the increase is 6.5 to 6.8 units per atom substituted. The optical constants of the salts have been accurately determined.

E. H. R.

Action of Oxygen on the Precipitation of Metals from Cyanide Solutions. OLIVER P. WATTS (*Chem. Met. Eng.*, 1918, 19, 652—653; from *Chem. Zentr.*, 1919, i, 811).—According to Crowe (*Chem. Met. Eng.*, 1918, 19, 283), the precipitation of gold is caused by hydrogen liberated by the zinc, so that removal of dissolved air from the cyanide solution acts favourably, since it prevents the loss of reducing agent by oxidation. The author, on the other hand, is of opinion that the gold is directly precipitated from its solutions by zinc in the same manner as is copper from copper sulphate solution. The solution of zinc in sodium cyanide only differs from its solution in copper sulphate in that hydrogen is liberated in place of copper. The presence of oxygen is necessary for the rapid solution of zinc or other metals in cyanide solutions, whilst it has no influence on the solution of zinc in copper sulphate. Two simultaneous actions occur when zinc is placed in a dilute solution of cyanide containing gold. A portion of the zinc is dissolved by the double cyanide with precipitation of gold, whilst another portion is dissolved by the sodium cyanide with evolution of hydrogen; only the former action is useful in the separation of gold. For every gram of hydrogen evolved, 32.5 grams of zinc are dissolved without precipitation of gold, whilst, also, the excess of cyanide with which the zinc reacts is not profitably utilised. This undesired solution of zinc is limited by the content of oxygen or air, which oxidises the polarising deposit of hydrogen. Not only does dissolved air cause a loss of zinc, but it also diminishes the

yield by expediting the re-solution of the precipitated gold in the same manner as it promotes the solution of metals in the treatment of ores with cyanide solutions.

H. W.

Mineralogical Chemistry.

Theory of Magmatic Mineral-forming Agents. JOHANN JAKOB (*Zeitsch. anorg. Chem.*, 1919, **106**, 229—267).—An important part in mineral and rock formation has undoubtedly been played by the gaseous and more or less easily volatile substances present in the magma. Among these mineral-forming agents water is by far the most important; other agents discussed include hydrogen sulphide, hydrogen fluoride, the oxides of carbon, sulphur dioxide, titanium dioxide, and a number of the less common metallic and non-metallic oxides. A precise definition of a mineral-forming agent cannot be given, but it must possess the property of forming additive compounds with other substances present in the fluid magma. These compounds are supposed to be of the co-ordinated type and generally to form mobile, complex ions. Through the interaction of these complex ions in the magma the different minerals are formed. For the purpose of discussion, the magma is considered as a highly concentrated solution of the other constituents in the mineral-forming agent; for example, in the case of water, as an aqueous solution. Hydrated forms of the different oxides present are probably produced, in which the elements can be supposed to exert the maximum co-ordinating power, with formation of such compounds as $[(\text{H}_2\text{O})_2\text{Si}(\text{OH}\cdot\text{OH})_4]\text{H}_4$ and $[\text{Mg}(\text{OH})_2(\text{OH}_2)_4]$.

At the high temperature of the magma, water is comparatively highly dissociated, and the hydrogen and hydroxyl ions combine with the hydrated compounds to form complex hydrated ions, through the interaction of which the different minerals are formed. New formulæ of the co-ordinated type are suggested for some of the complex silicates. The same ideas are applied to the discussion of rock metamorphosis.

E. H. R.

Chemistry of Coal. I. Action of Pyridine on the Coal Substance. WILLIAM A. BONE and REGINALD J. SARJANT (*Proc. Roy. Soc.*, 1919, [A], **96**, 119—136).—Experiments on the solvent action of pyridine on coal have shown that the presence of oxygen has an important retarding action, varying with the nature of the coal, on the extraction process. This is due to the oxidation of the coal substance which may occur before or during the extraction. Previous oxygenation of the coal renders it much less susceptible to the solvent action of pyridine. The presence of water in the pyridine also has a retarding influence. To obtain concordant results

it is therefore necessary to exclude air, to use carefully dried and purified pyridine, and in addition to grind the coal to a standard mesh and to have a standard form of extraction apparatus. Such an apparatus is described in the present paper. The picolines extract about the same amount as pyridine, but, owing to their greater instability, they are less suitable as solvents. When the pyridine extract, which may amount to more than 30% by weight of the original coal, is again extracted with chloroform about 50% is dissolved. According to Clarke and Wheeler (T., 1913, **103**, 1704), the chloroform effects a complete separation of the resinic from the cellulosic constituents of the coal, but the analysis of the pyridine-chloroform extract does not warrant the view that it represents even an approximately pure coal resin. [See also *J. Soc. Chem. Ind.*, 1919, October.] E. H. R.

Relations between Tridymite and Cristobalite. C. N. FENNER (*J. Soc. Glass Tech.*, 1919, **3**, 116—125).—The author disputes the conclusion of Rees (*J. Soc. Glass Tech.*, 1918, **2**, 253), Scott (*ibid.*, 1918, **2**, Abs. 169), and Le Chatelier (A., 1917, ii, 97) that tridymite is more stable than cristobalite at temperatures above 1480°. He cites numerous experiments to the contrary, and states that in the course of a long series of experiments, no obvious loophole was left by which it was possible to escape the conclusions regarding the stability relations which have been drawn. At temperatures above 1470±10°, quartz, tridymite, and amorphous silica have repeatedly and unequivocally been converted into cristobalite; between 1470±10° and 870±10°, quartz, cristobalite, and amorphous silica have similarly been converted into tridymite; and below 870±10° tridymite, cristobalite, and amorphous silica have been converted into quartz. These relations have been confirmed again and again. Moreover, recent work by Ferguson and Merwin (A., 1918, ii, 362) has indicated that the melting point of tridymite is considerably lower than that of cristobalite. It follows necessarily from this observation that cristobalite is the high-temperature form. [See *J. Soc. Chem. Ind.*, 1919, 722A.] A. B. S.

Composition of Bornite. AUSTIN F. ROGERS (*Science, New York*, 1915, [N.S.], **42**, 386—388).—The formula proposed by Kraus and Goldsberry (A., 1914, ii, 570; compare Allen, A., 1916, ii, 391) is discussed. Fifty-nine published analyses are plotted on a triangular diagram; they all fall near the line CuFeS_2 to Cu_2S , with the greatest cluster near Cu_5FeS_4 , and lower and upper limits near Cu_3FeS_3 and $\text{Cu}_{12}\text{Fe}_3\text{S}_9$. The most probable explanation of the variations in composition of bornite is that of a solid solution of Cu_2S in Cu_3FeS_3 , the formula being written as $\text{Cu}_3\text{FeS}_3(\text{Cu}_2\text{S})_x$. L. J. S.

Scapolite of Gem Quality from the Pegmatites of Madagascar. A. LACROIX (*Compt. rend.*, 1919, **169**, 261—264).—Transparent, yellow scapolite occurs as corroded and striated square prisms several cm. in length, together with beryl, euxenite, and monazite, in a potash-pegmatite at Tsarasaotra on the Tsibohaina

river. D 2·67. Optically uniaxial and negative with slight pleochroism, $\omega_{Na} = 1·5698$, $\epsilon_{Na} = 1·5490$, $\omega - \epsilon = 0·0208$. It is father harder (H $6\frac{1}{2}$) than ordinary scapolite and shows no cleavage, the fracture being conchoidal. Estimations of some of the more unusual constituents gave (compare this vol., ii, 163):

CO ₂ .	Cl.	F.	SO ₃ .	SrO.	FeO.	Fe ₂ O ₃ .
2·52—2·71	1·59	0·37	nil	0·09	0·90	0·11

Cut stones resemble certain beryls in appearance and in some of their characters; there is, however, a marked difference in the strength of the double refraction and in the hardness. L. J. S.

Analytical Chemistry.

Normal Temperature for the Standardisation of Chemical Apparatus, etc. WALTER BLOCK (*Chem. Zeit.*, 1919, **43**, 477—479).—The author discusses the subject regarding the temperature at which laboratory apparatus should be standardised, and considers that 20° would be more suitable and convenient than 15°, a temperature now usually taken as the normal in chemistry and physics. W. P. S.

Automatic Apparatus for Gas Analysis. OLOF RODHE (*Svensk. Kem. Tidskr.*, 1919, **31**, 5—14).—The apparatus automatically estimates and records by means of a kymograph the relative amounts of oxygen, carbon dioxide, carbon monoxide, hydrogen, methane, or other constituent in a gas. It is constructed on the principle of a train of absorption, combustion, and measuring units without taps. One or more aggregates may be used and the flow of gas may be shunted from one to another, depending on the constituent considered significant in the control work, for example, carbon monoxide or hydrogen in a water-gas plant, carbon dioxide or oxygen in a lime or cement kiln, etc.

CHEMICAL ABSTRACTS.

Gas Burette. PAUL NICOLARDOT and GUSTAVE PREVOT (*Ann. Falsif.*, 1919, **12**, 140—145).—The apparatus consists of a graduated tube, about 2 cm. in diameter, the upper part of which is widened out so as to form a cylinder of about 6 cm. in diameter and having a capacity three to four times that of the narrow tube; the wide portion of the burette is also graduated. The two ends of the burette are provided with taps. The capacity of the whole burette may be from 200 to 400 c.c. W. P. S.

Apparatus for the Collection of Gases in Spring Waters, etc. O. HACKL (*Chem. Zeit.*, 1919, **43**, 421—422).—A wide-mouthed bottle is closed with a rubber stopper through which pass the stem of a funnel and a short length of glass tubing.

To collect gases rising from a natural spring, the bottle is filled by immersing it in the water, then inverted so that the bubbles of gas are collected by the funnel and pass into the bottle, the water leaving the latter through the glass tube. When the bottle is full of gas, the stopper is removed while the bottle is still immersed in the water, and another stopper carrying two tubes is inserted; the outer ends of these tubes are closed by short lengths of rubber tubing carrying pinch-cocks. The gases are transferred to a Hempel apparatus by means of these tubes. A Bunsen collecting tube may also be used for the purpose, the end being closed with a rubber stopper carrying a funnel and side-tube; the stem of the funnel is provided with a length of rubber and glass tubing which extends below a constriction in the collecting tube just below the stopper.

W. P. S.

The Boiling Point as a Criterion of Purity and a New Apparatus for its Determination without Correction for the Thermometer. THEODOR PAUL and KARL SCHANTZ (*Arch. Pharm.*, 1919, 257, 87—129).—The methods for the determination of the boiling point prescribed in the fifth edition of the German Pharmacopœia, when required for purposes of identification and as a means of controlling purity, have been critically examined. The latter method (distillation of a measured volume of the liquid under definite conditions) only gives a rough approximation of the true b. p., so that the data recorded in the Pharmacopœia do not generally coincide with the actual b. p.'s of the respective liquids even when these in other respects satisfy the pharmaceutical requirements. Further, the influences of variation in the barometric height and of the projecting thread of the thermometer are not taken into consideration.

The influence of common impurities on the b. p.'s of pharmaceutical preparations has been investigated. Addition of water lowers the b. p. of ethyl ether until it is present to the extent of 1.3%, after which no further depression occurs; ethyl alcohol, on the other hand, raises the b. p. of ethyl ether, and a specimen of the latter containing 1.15% of ethyl alcohol and 1.8% of water (by weight) has the same b. p. as pure ethyl ether. The depression of the b. p. of chloroform by addition of ethyl alcohol has been further studied; water produces a similar effect, but the quantitative relationships could not be studied by reason of peculiar condensation phenomena. The b. p. of ethyl bromide is depressed by the presence of ethyl alcohol or water, the effect of which when simultaneously present is additive. The presence of benzoic acid elevates the b. p. of benzaldehyde.

The boiling points for different barometric pressures, calculated according to the formula $t = t_0 - (t_0 + 273) \cdot c \cdot (760 - h)$, agree satisfactorily with the observed values.

A new apparatus is described which allows the determination of the boiling point of a liquid at constant composition and during fractional distillation. The vessel consists of a stout-walled test-tube about 18 cm. high and 20 mm. internal diameter which con-

tains a layer, 3 cm. high, of beads. So much liquid (about 15 c.c.) is used that its surface is about 3.5 cm. above the beads. A column is attached to the test-tube consisting of a vapour tube (23 cm. \times 11 mm.) which is surrounded by a vapour jacket (20—22 cm. \times 20 mm.), in which the thermometer is supported. The jacket and tube are sealed together about 14 cm. above the lower end of the tube. Immediately above the junction, a side-tube, which can be connected with a condenser, and a small bent tube, which is also sealed in to the lower portion of the vapour jacket and permits the condensed liquid to return to the still, are attached. The vessel is placed in the middle of an asbestos sheet in which a hole, 2 cm. in diameter, has been cut, the opening being closed from below by copper gauze. The asbestos sheet must be sufficiently large to prevent the radiant heat from the burner from affecting the thermometer. For liquids which boil above 100°, it is advisable to protect the boiling tube with an air-jacket. The thermometer is inserted in such a manner that the thread is completely surrounded by the vapour. The height of the flame is so adjusted that the liquid just boils vigorously. The b. p. is read when the thermometer does not show a variation greater than one-tenth of a degree during three minutes. By rotating the condenser through 180°, the apparatus may be used either for refluxing or for distillation. H. W.

Substitute for Hydrogen Sulphide Water. BAYER (*Pharm. Post*, 1918, 354; *Schweiz. Apoth. Ztg.*, 1919, 57, 140).—Ten grams of sodium sulphide are dissolved in 50 c.c. of water + 50 c.c. of glycerol. No special apparatus is required.

CHEMICAL ABSTRACTS.

Stabilising Normal Alkali Solution. WINKLER (*Pharm. Post*, 1918, 354; *Schweiz. Apoth. Ztg.*, 1919, 57, 140).—The absorption of carbon dioxide by *N*-alkali may be reduced to a minimum by replacing 30% of the water used by 30% of glycerol. This also prevents the sticking of glass stoppers.

CHEMICAL ABSTRACTS.

Conditions for Obtaining Pure Sodium Carbonate for Standardising Acid and Applicability of Crystallised Oxalic Acid in place of the Anhydrous Acid as a Titration Standard. HERMANN KUNZ-KRAUSE and RUDOLF RICHTER (*Arch. Pharm.*, 1917, 255, 540—549).—If stirred with a platinum wire, sodium hydrogen carbonate is converted quantitatively into sodium carbonate at 250°. Microcrystalline oxalic acid (+ 2H₂O) may be used for the direct preparation of standard acid; its solutions keep their titre if protected from the light. [See *J. Soc. Chem. Ind.*, 1919, October.] T. H. P.

Liquid Ammonia-Sodium Method for [Estimating Halogens in Organic Compounds, the Formation of Cyanide and the Method of Removing [it] from the Solution. CHARLES WILLIAM CLIFFORD (*J. Amer. Chem. Soc.*, 1919, 41, 1051—1060).—This method of estimating halogens in organic com-

pounds, due to Chablay (A., 1914, i, 918), consists in adding liquid ammonia to a small quantity of the substance in a Dewar vessel, and then metallic sodium until a permanent blue colour is produced. The halogen is thereby converted into the sodium haloid. The excess of ammonia is allowed to evaporate, and the excess of sodium is removed by treatment with alcohol. The residue is dissolved in water acidified with nitric acid, treated with excess of standard silver nitrate, and the excess of silver titrated with sodium thiocyanate. This reaction has been investigated as to its trustworthiness. It is found that in many cases cyanide is also formed, and consequently the procedure as outlined above cannot, in many cases, be carried out without the possibility of error. On acidifying, only a portion of the hydrocyanic acid which may have been formed is expelled. At best, the decomposition of silver cyanide and elimination of cyanide by boiling in diluted nitric acid are only approximately quantitative. The percentage of cyanide formed is not a constant for each substance under the conditions of analysis. Treatment with sodium in liquid ammonia completely removes any halogen present in organic compounds, and the resulting haloid is separated quantitatively from any cyanide present by acidifying the solution with acetic acid and boiling. J. F. S.

Adaptation of the Mohr Volumetric Method to the General Estimation of Chlorine. LESTER YODER (*J. Ind. Eng. Chem.*, 1919, 11, 755).—The following procedure is recommended for the estimation of chlorine in organic substances. A suitable quantity of the sample is treated with 5 c.c. of 30% calcium acetate solution and sufficient water to form a moist mass, the mixture is evaporated to dryness, and incinerated below 450°. The cooled residue is moistened with a few c.c. of 10% ferric acetate solution, again dried, and ignited below 450°. The residue is dissolved in water, the solution filtered, the filter washed with hot water, the filtrate evaporated to dryness, and this residue dissolved in a small quantity of water. After the addition of a few drops of potassium chromate solution, the chloride is titrated with standardised silver nitrate solution. The calcium acetate fixes free chlorine, precipitates carbonates, and neutralises the filtrate; the ferric acetate precipitates phosphates, and the excess is converted into insoluble ferric oxide during the ignition. W. P. S.

Simplification of Kjeldahl's Method in Clinical Chemistry. E. PITTARELLI (*Riv. crit. clin. med.*, 1919; from *J. Pharm. Chim.*, 1919, [vii], 20, 32—34).—To estimate nitrogen in urine, 1 c.c. of a 10% solution of the sample is digested with 2 c.c. of sulphuric acid and one drop of phenol, a small quantity of potassium persulphate being added towards the end of the reaction. The mixture is then neutralised, treated with 10 c.c. of a mixture of three volumes of saturated sodium hydrogen carbonate solution and one volume of saturated mercuric chloride solution, the whole

diluted to 250 c.c., and the turbidity compared with that obtained with a known quantity of ammonia.

W. P. S.

Systematic Procedure for the Detection of Acids of Group I. LOUIS J. CURTMAN and DAVID HART (*Chem. News*, 1919, **119**, 25—29, 37—40).—A scheme is proposed by means of which the acids of group I may be systematically detected and the relative amounts approximately estimated. The chief steps in the scheme are (a) a preliminary precipitation of all the acids of group I with a mixture of barium and calcium chlorides, (b) treatment of the precipitate with hydrochloric acid to dissolve all but the sulphate, (c) oxidation with hydrogen peroxide to convert sulphite into sulphate and precipitation of the latter with barium chloride, (d) removal of barium from the solution with ammonium sulphate, (e) separation of fluoride, arsenate, and phosphate from borate and tartrate in alkaline solution in the presence of sufficient ammonium salts, (f) removal of oxalate and fluoride from arsenate and phosphate in an acetic acid solution containing an excess of calcium ions, (g) reduction of arsenate to arsenite with sulphur dioxide and separation from phosphate by hydrogen sulphide in hydrochloric acid solution, (h) separate tests for carbonates and chromates, and (i) separate tests for the determination of the state of oxidation of the arsenic. Very full details of the effect of the various acids on one another in the several stages of the separation are given, and by means of these the method is shown to be trustworthy.

J. F. S.

Influence of Temporary Hardness on the Estimation of Chlorides in Water. W. HERBIG (*Zeitsch. angew. Chem.*, 1919, **32**, 216).—The temporary hardness of water is without influence on the estimation of chlorides by Mohr's method, and consequently the procedure adopted by Lombard (A., 1913, ii, 1068) is unnecessary.

W. P. S.

Rapid Estimation of Nitric Acid. LUCIEN MAUGÉ (*L'Ind. chimique*, 1918, **8**, 255—256; from *Chem. Zentr.*, 1919, ii, 720).—When nitric acid is added to a solution of ferrous sulphate acidified with sulphuric acid, oxidation of a portion of the salt occurs, accompanied by formation of nitric oxide, which yields the intensely brown additive compound with the excess of ferrous sulphate; on further addition of nitric acid, the colour disappears as soon as the ferrous sulphate is completely oxidised: $6\text{FeSO}_4 + 3\text{H}_2\text{SO}_4 + 2\text{HNO}_3 = 3\text{Fe}_2(\text{SO}_4)_3 + 2\text{NO} + 4\text{H}_2\text{O}$. The discharge of the colour is sufficiently sharp for the process to be applied to the volumetric estimation of nitric acid. The solution of ferrous sulphate contains 66.66 grams $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ per litre, and is standardised by permanganate; 10 c.c. of this solution are heated with 50 c.c. of sulphuric acid (60—66 Bé.) and titrated with the nitric acid under investigation until decolorised.

H. W.

Estimation of Phosphoric Acid as Magnesium Pyrophosphate. D. BALAREFF (*Zeitsch. anorg. Chem.*, 1919, 106, 268—280).—In the estimation of phosphoric acid by the double precipitation method, although trustworthy results are obtained, the ignited precipitate is not pure, but contains excess of magnesium and too little phosphoric acid (A., 1918, ii, 406). Neubauer's method for the estimation of magnesium, in which a solution of phosphoric acid is added to the magnesium solution, gives high results when the ammonia is added quickly for the second precipitation, but when the ammonia is added slowly the results approximate to those obtained by Schmitz's method (*loc. cit.*). The use of an alkali phosphate in place of phosphoric acid causes the results to be high on account of the precipitation of alkali magnesium phosphate.

Further experiments on Schmitz's method for phosphoric acid have been made. In this method excess of magnesium chloride is added to the phosphate solution, together with a quantity of ammonium chloride. Sufficient ammonia is then added to the hot solution to cause precipitation as the solution cools. Although this method gives consistent results with widely varying conditions of concentration and proportions of the reacting substances, the conditions for obtaining a pure precipitate of magnesium ammonium phosphate are very circumscribed. More concentrated solutions give purer products, and the purity is increased by diminishing as far as possible the quantity of ammonia used. High results are obtained if too little ammonium chloride is used and the solution is not stirred during the precipitation of the magnesium ammonium phosphate.

With regard to the nature of the impurity accompanying the precipitate, the conditions favouring an impure precipitate are those which would be expected to favour the formation of the compounds $\text{Mg}[(\text{NH}_4)_2\text{PO}_4]_2$ and $\text{Mg}_3(\text{PO}_4)_2$. The former salt, however, should give, on ignition, magnesium metaphosphate, insoluble in hydrochloric acid, but it is found that the precipitate obtained by Schmitz's method is completely soluble, although precipitates formed in the cold contain much metaphosphate (A., 1918, ii, 332). Possibly a second form of metaphosphate exists, soluble in hydrochloric acid, or it may be that other complex compounds are precipitated instead of the above diphosphate. There are grounds for supposing that magnesium ammonium phosphate when ignited undergoes secondary decompositions which have a connexion with the incandescence and blackening which sometimes occur on ignition (compare A., 1917, ii, 90). All experiments on this phenomenon appear to have been made with samples of magnesium ammonium phosphate of doubtful purity, and it is impossible yet to come to any satisfactory conclusions. E. H. R.

Modified Method of Estimating Arsenic as Ammonium Magnesium Arsenate. O. BAILLY (*J. Pharm. Chim.*, 1919, [vii], 20, 55—58).—The ammonium magnesium arsenate precipitate, obtained in the usual way, is washed with dilute ammonia, then

with alcohol to remove free ammonia, and titrated with $N/2$ -acid, using methyl-orange as indicator. Each c.c. of $N/2$ -acid is equivalent to 0.01875 gram of arsenic. W. P. S.

Iodometric Estimation of Arsenic Acid. I. M. KOLTHOFF (*Pharm. Weekblad*, 1919, **56**, 1322—1326).—The reaction $\text{As}_2\text{O}_3 + 4\text{HI} \rightleftharpoons \text{As}_2\text{O}_3 + 2\text{I}_2 + 2\text{H}_2\text{O}$ proceeds from left to right only in strongly acid solution. Accurate titration results are obtained for arsenate concentrations of $N/5$ to $N/10$ with a minimum concentration of hydrochloric acid of $4N$ in the mixture. For more dilute arsenate solutions ($N/50$), a minimum hydrochloric acid concentration of $4.5N$ is required. After addition of the iodide and the acid to the arsenate solution, five minutes must elapse before titration with thiosulphate.

Molybdate, tungstate, vanadate, manganous, ferrous, uranyl, and chromic ions appear to have no catalytic effect on the reaction. W. S. M.

Estimation of Free Alkali or Alkali Carbonate Alone or in the Presence of Alkali Hypochlorite. W. MESTREZAT (*J. Pharm. Chim.*, 1919, [vii], **20**, 9—14. Compare this vol., ii, 79).—Alkali hypochlorite solution, containing no free alkali hydroxide or carbonate, is neutral towards reagents after the hypochloride has been decomposed by thiosulphate. Free alkali or alkali carbonate in such solution can, therefore, be titrated; alkali carbonates, in the cold and in concentration not exceeding $N/80$, are alkaline towards phenolphthalein, but the alkalinity disappears when the titration has proceeded to the formation of alkali hydrogen carbonate. W. P. S.

Estimation of Free Alkali Hydroxide and Carbonate in Alkali Hypochlorite Solution. PHILIBERT (*J. Pharm. Chim.*, 1919, [vii], **20**, 52—55. Compare this vol., ii, 79).—A reply to Mestrezat (preceding abstract). The author maintains the trustworthiness of the iodo-acidimetric method. W. P. S.

Estimation of Very Small Amounts of Calcium, Magnesium, and Phosphorus in Animal Substances. L. DIENES (*Biochem. Zeitsch.*, 1919, **95**, 131—145).—The methods described are essentially those usually employed, namely, the estimation of calcium as oxalate by titration with permanganate, the estimation of magnesium by the determination of the phosphorus present in the precipitated magnesium ammonium phosphate, and the estimation of phosphorus by titration of the precipitated ammonium phosphomolybdate with standard alkali. The technique of the methods has been suitably modified for the manipulation of very small quantities. J. C. D.

Estimation of Zinc and Calcium in the Presence of Lead. ERNEST NYMAN (*Chem. News*, 1919, **119**, 75—76).—Zinc and calcium may be estimated in the presence of lead, in such mixtures as are frequently found in pigments, by the following method. An

acid solution of the salts is treated with ammonia until strongly alkaline and then acidified with acetic acid. Should a precipitate be formed it is dissolved by the addition of a few grams of ammonium acetate. When a clear solution is obtained the solution is made slightly alkaline with ammonia and titrated at 70—80° with standard potassium ferrocyanide solution, using an acid solution of uranyl acetate as external indicator. In this way the zinc may be accurately estimated. To estimate the calcium a faintly alkaline solution is prepared as described above, and the calcium precipitated by the addition of an excess of ammonium oxalate. J. F. S.

Alkalimetric Estimation of Small Amounts of Magnesium.

P. L. HIBBARD (*J. Ind. Eng. Chem.*, 1919, **11**, 753—754).—A method described previously by Bruckmiller (A., 1917, ii, 271) for the titration of ammonium magnesium phosphate is modified by the author in order to render it applicable to the estimation of small amounts of magnesium (5 mg., or less) such as are found in soil extracts. The principal modifications introduced are the use of a Gooch crucible for filtration, whereby the precipitate may be washed with the least possible quantity of solution, washing the precipitate with alcohol and then with a cold saturated ammonium magnesium phosphate solution, and the use of methyl-red as indicator in the titration. W. P. S.

A Colour Reaction which may be Used for the Detection of Mercury in Mercury Compounds.

ARTHUR ABELMANN (*Pharm. Zentr.-h.*, 1919, **60**, 247—248).—The following reaction is given by mercury salts and even by organic mercury compounds in which the mercury does not react with hydrogen sulphide. A solution or suspension of the mercury compound is treated with a drop of dilute nitric acid and a moderate quantity of ferrous sulphate solution, and concentrated sulphuric acid is added so as to form a layer under the mixture; a reddish-violet ring is formed at once at the junction of the two liquids. After some time the usual brown ring (nitric acid reaction) appears above the violet ring. W. P. S.

Volumetric Estimation of Mercury Salts and the Estimation of Mercury in Mercury Chloride Compresses.

F. UTZ (*Pharm. Zentr.-h.*, 1919, **60**, 301—302).—A method described recently by Adanti (A., 1916, ii, 579) was proposed originally by Rupp (A., 1905, ii, 484; 1906, ii, 902), and applied by Utz (A., 1907, ii, 400). W. P. S.

Estimation of Iron in Iron Ores by means of Permanganate.

L. BRANDT (*Chem. Zeit.*, 1919, **43**, 394—397).—The influence of colloidal silica on the titration of ferrous salts with permanganate (compare Schwartz and Rolfes, this vol., ii, 170) in hydrochloric acid solution is not due to its inhibiting action on the reaction between hydrochloric acid and permanganate, since the same effect is noticed in sulphuric acid solutions. The decreased

amount of permanganate required for the titration in the presence of colloidal silica appears to be due to dissolved and atmospheric oxygen, the silica acting as a catalyst in the oxygen-ferrous salt-permanganate reaction. Silica has no influence on the reaction between oxygen and ferrous salts in the absence of permanganate.

W. P. S.

Analysis of Steel. A. TRAVERS (*Ann. Chim.*, 1919, [ix], 11, 17—128. Compare this vol., ii, 81, 300).—An exhaustive résumé of methods for the estimation of the usual constituents of steels; the original should be consulted for the many methods which are given in detail. [See, further, *J. Soc. Chem. Ind.*, 724A.]

W. P. S.

Estimation of Iron, Zinc, Copper, and Aluminium in Aluminium Alloys. PAUL HOLMSEN (*Tidskr. Kemi. Farm. Ter.*, 1919, 16, 62—63).—The separation of copper, iron, aluminium, and zinc is effected by treating the sample with 30% sodium hydroxide solution, using 50 c.c. for a 3-gram sample. When the aluminium and zinc are in solution, water is added, and the residue of iron and copper removed by filtration. Aluminium is separated from zinc and iron from copper by adding ammonia to the acid solutions of these two pairs, and the four metals are estimated by well-known methods.

CHEMICAL ABSTRACTS.

Electrolytic Estimation of Nickel and Cobalt. MOTOOKI MATSUI and TADASU NAKAZAWA (*J. Tokyo Chem. Soc.*, 1919, 40, 339—349).—Nickel and cobalt can be precipitated quantitatively from their dimethylglyoxime salts by electrolysis. The following modification is therefore substituted for the usual method. To the mixture of nickel and cobalt, sodium acetate and an excess of dimethylglyoxime (0.2 gram) are added until the precipitation of nickel is complete. The precipitate is washed, dissolved in sodium hydroxide (4.8 grams), and estimated by electrolysis. To the filtrate is added sodium hydroxide, and the cobalt estimated similarly. When the amount of nickel exceeds 0.058 gram in 100 c.c., an addition at the positive pole of a few drops of a mixture containing 5 c.c. of glycerol, 45 c.c. of alcohol, and 50 c.c. of water is necessary in order to prevent deposition of the oxide at the pole. When cobalt is present in a high concentration, the similar oxide deposit can be prevented if aqueous ammonia (50 c.c.) containing 2 grams of ammonium sulphate, to increase the conductivity, is substituted for sodium hydroxide. From a mixture containing 0.0102 gram of nickel and 0.1836 gram of cobalt made up to 100 c.c., using 3.2 volts for nickel, 3.8 volts for cobalt, with one ampere current, were obtained 0.0100 gram of nickel after 2.5 hours and 0.1834 gram of cobalt after 3.3 hours at the ordinary temperature. The temperature should always be kept under 50°, otherwise the positive pole will be coated with the oxide.

CHEMICAL ABSTRACTS.

Analysis of Alloys of Tin. ARCHIBALD CRAIG (*J. Ind. Eng. Chem.*, 1919, 11, 750—753).—A discussion of the conditions giving the most trustworthy results in the analysis of tin alloys by the nitric acid separation method; the processes for the various separations and purification of the precipitates, etc., are given in detail. W. P. S.

Separation of Tin, Antimony, and Arsenic by Plato's Method. WILLY HARTMANN (*Zetsch. anal. Chem.*, 1919, 58, 148—156).—Modifications of this method (A., 1910, ii, 903) are described. After antimony and arsenic have been distilled, as in the original method, the residue is treated with a mixture of hydrobromic and hydrochloric acids, and the tin distilled at 130° to 140° in a current of carbon dioxide. Arsenic is separated by treating the distillate, in the cold, with hydrogen sulphide; the arsenic trisulphide is collected on a filter, and the antimony is also precipitated as sulphide after the filtrate has been neutralised with ammonia. W. P. S.

Estimation of Cerium in the Presence of other Rare Earths by Precipitation as Ceric Iodate. PAUL H. M.-P. BRINTON and C. JAMES (*J. Amer. Chem. Soc.*, 1919, 41, 1080—1085).—Solutions containing rare earth nitrates (thorium having been removed) may be quantitatively analysed for cerium as follows: the solution is treated with half its volume of nitric acid; the whole solution at this stage should not be more than 75 c.c., and the amount of cerium oxide should not exceed 0.15 gram; 0.5 gram of potassium bromate is added, and when it has dissolved ten to fifteen times the theoretical quantity of potassium iodate is added in nitric acid solution (100 grams iodate, 333 grams acid) with constant stirring. The ceric iodate is allowed to settle and filtered on a paper of close texture. After draining, the precipitate is washed back into the beaker by means of a solution containing 8 grams of potassium iodate and 50 c.c. of nitric acid per litre. The precipitate is well mixed with the washing solution and brought back on to the same filter paper. It is then rinsed back into the beaker with hot water, heated to boiling, and treated drop by drop with nitric acid until it is entirely dissolved. To this solution, 0.25 gram of potassium bromate and as much iodate as was previously used are added. The precipitate is allowed to settle and then filtered through the same filter paper, and washed once with the washing solution. It is brought back into the beaker, well stirred, and again filtered and washed with three small portions of the washing solution. The filter paper and precipitate are now dropped into the original beaker, and 5—8 grams of oxalic acid and 50 c.c. of water are added. The beaker is covered and gently heated, and then boiled until iodine is no longer expelled. The precipitate is kept several hours,

filtered, washed, dried, and ignited to oxide, which is weighed. This method is trustworthy even in the presence of large quantities of the other rare earths.

J. F. S.

Electrometric Titration of Vanadium. Selective Oxidation of Vanadyl Salts in Presence of Chromic Salts. G. L. KELLEY, J. A. WILEY, R. T. BOHN, and W. C. WRIGHT (*J. Ind. Eng. Chem.*, 1919, 11, 632—634).—For the estimation of small quantities of vanadium in steel by the method of electrometric titration (A., 1917, ii, 512), the sample is dissolved in sulphuric acid and the vanadium oxidised by boiling with nitric acid under specified conditions. This oxidises vanadyl compounds to the extent of about 99% without oxidising chromic compounds. The liquid is then cooled and titrated by the electrometric method with ferrous ammonium sulphate which has been standardised against potassium dichromate solution. A correction is subsequently made for the 1% of unoxidised vanadium. In estimating chromium in chrome-vanadium steels, the solution, obtained as described, is oxidised with nitric acid, and then treated with silver nitrate solution and ammonium persulphate solution, boiled to decompose the excess of persulphate, acidified with hydrochloric acid, boiled and cooled, and the chromium and vanadium titrated together. The vanadium end-point is that previously described (*loc. cit.*). The result for vanadium is expressed in its equivalent of chromium and deducted from the total dichromate solution used in the titration of the chromium and vanadium. [See also *J. Soc. Chem. Ind.*, 1919, 583A.]

C. A. M.

Microchemical Reaction of Various Bismuth Compounds. G. DENIGÈS (*Bull. Soc. pharm. Bordeaux*, 1919; from *Ann. Chim. anal.*, 1919, [ii], 1, 213—214).—A drop of dilute hydrochloric acid and a drop of 5% hexamethylenetetramine solution are mixed on a microscope slide, and a drop of a bismuth solution or a small particle of an insoluble bismuth compound is brought into contact with the mixture. On examining the preparation under the microscope (a cover-glass is not used), characteristic crystals are observed, mainly at the point of contact. The crystals are colourless and have the form of hexahedra, hexagonal plates, dodecahedra, or rhombic octahedra. The crystals may be obtained from practically all bismuth compounds.

W. P. S.

Electroanalysis of Bismuth and its Ores. MANZO NAKAO (*J. Pharm. Soc. Japan*, 1919, No. 446, 275—307).—The formation of spongy and loose granular precipitates at the negative pole is one of the sources of error and difficulties in the electroanalysis of bismuth. Sand's method, although it prevents the formation of the spongy deposit, does not produce sufficiently permanent precipitates that will not easily peel off on drying. The

author modifies the methods used by Sand and Fischer by proposing the use of a very small amount of colloidal substances. An addition of 1 mg. of gum arabic to 100 c.c. of the solution not only produces a more permanent precipitate of bismuth, but also gives a quantitative yield in ten minutes. In separating bismuth from copper, the formaldehyde used by Sand to prevent the formation of bismuth oxide is replaced by borax and hydroxylamine sulphate. The best result is obtained by using sodium tartrate 4 grams, sodium hydroxide 4 grams, potassium cyanate 3.5 grams, hydroxylamine 0.5—1 gram, borax 2—1 grams, made up to 120 c.c., stirring at the rate of 1200 revolutions per minute at 65° for twenty minutes, employing 0.4—0.2 ampere, and maintaining 1.2—1.7 volts at the poles. Under this condition, 0.3131 gram out of 0.3130 of bismuth is obtained in the separation from 0.3 gram of copper. In estimating bismuth in bismuth ores, after removing tin and lead, instead of using hydrogen sulphide, ammonia and ammonium chloride are employed, the mass is dissolved in as little nitric acid as possible, and 4 grams of tartrate, 2 grams of sodium hydroxide, 5 grams of potassium cyanate, and 1 gram of hydroxylamine are added, the volume being made up to 120 c.c., and a current of 1.2 volts used. When the voltage exceeds 1.2, the current is changed to 0.1 ampere; above 1.8 volts, 2 amperes, and finally 0.5 ampere, of current are used for thirty-five minutes (70—80°), stirring at the rate of 1000 revolutions per minute.

CHEMICAL ABSTRACTS.

Estimation of the Inorganic Constituents of Blood and other Physiological Material. ISIDOR GREENWALD (*J. Biol. Chem.*, 1919, **38**, 439—440).—Proteins and fats are removed from the blood by precipitation with picric acid. The oxidation of the filtrate for the purpose of estimating the inorganic constituents is then an easy matter. J. C. D.

Use of the Critical Temperature of Solution in Aniline in the Summary Analysis of a Petroleum. G. CHAVANNE and L. J. SIMON (*Compt. rend.*, 1919, **169**, 70—73).—By summary analysis, the authors mean a determination of the percentage of aromatic hydrocarbons (*Ar*), saturated cyclic hydrocarbons (*C*), and acyclic hydrocarbons (*Ac*) present in the petroleum. The critical temperatures of solution of the petroleum in aniline are determined before and after its treatment with a mixture of sulphuric and nitric acids to remove the aromatic hydrocarbons, the two values obtained being respectively T_1 and T_2 . Then the respective percentages may be calculated from the three formulæ $Ar = 1.18(T_2 - T_1)$, $C = [72 - (T_2 + 0.2)](100 - Ar)/(72 - 39.5)$, and $Ac = 100 - Ar - C$. These formulæ contain all necessary corrections except for the presence of ethylenic hydrocarbons. If these are present, for T_1 must be written $T_1 + 0.4E$, where E is the percentage of ethylenic hydrocarbons expressed as amylene. W. G.

Critical Temperatures of Solution in Aniline of Mixtures of Hydrocarbons. Application to the Analysis of Petroleum.

G. CHAVANNE and L. J. SIMON (*Compt. rend.*, 1919, **169**, 185—188. Compare preceding abstract).—A mixture of two acyclic hydrocarbons or a mixture of one acyclic and one saturated cyclic hydrocarbon obeys the law of additivity in so far as its critical temperature of solution in aniline is concerned, but a mixture of two saturated cyclic hydrocarbons does not obey this law. If to a mixture of hydrocarbons, devoid of aromatic hydrocarbons, benzene is added to an extent not exceeding 10—15%, then the depression of the critical temperature of solution in aniline is proportional to the percentage of benzene added, the ratio being 1:1·14. Similarly, for toluene the ratio is 1:1·19 and for xylene 1:1·24. The above results furnish the basis for the method of analysis of petroleum previously outlined (preceding abstract), it being necessary first to fractionate the petroleum so that there is only one saturated cyclic hydrocarbon in each fraction. W. G.

The Composition of some Asiatic Petroleums.

G. CHAVANNE and L. J. SIMON (*Compt. rend.*, 1919, **169**, 285—288).—Using the analytical method based on the critical temperature of solution in aniline, previously described (this vol., ii, 267; preceding abstracts), the authors have determined the composition of petroleums coming from Persia, Sumatra, and Borneo. The Persian and Sumatran petroleums are particularly rich in acyclic hydrocarbons. The Borneo petroleum was fractionated, and the different fractions were examined separately. Further details are given for the correction necessary in the calculation due to the presence of ethylenic hydrocarbons. W. G.

Estimation of Thiophen. PERCY E. SPIELMANN and S. P. SCHOTZ (*J. Soc. Chem. Ind.*, 1919, **38**, 188—189 τ).—A modified basic mercuric sulphate method is recommended for the estimation of thiophen in benzene. Two c.c. of the sample are shaken for three hours in a closed tube with 20 c.c. of basic mercuric sulphate solution (sulphuric acid, 20 c.c.; mercuric oxide, 5 grams; water, 100 c.c.). The precipitate formed is collected, washed with hot water, dried at 110°, and weighed; its weight multiplied by 0·0757 gives the amount of thiophen in 2 c.c. of benzene. Another, but less convenient, method consists in heating 10 c.c. of the benzene at 100° for fifteen minutes with 4 grams of basic mercuric acetate (glacial acetic acid, two parts; mercuric oxide, one part). After cooling, the precipitate is collected, washed with water, dried at 100°, and weighed. In this case, the factor is 0·07516. W. P. S.

Use of Refraction in Analysis. O. FAUST (*Zeitsch. anal. Chem.*, 1919, **58**, 145—148).—The refractometer may be used for estimating alcohol in mixtures of alcohol and water, provided that the amount of alcohol lies between 0 and 40%. The maximum refraction is given by alcohol of about 80%, and decreases as the

concentration rises or falls, so that between 50 and 100% there are always two mixtures having the same refraction. W. P. S.

Estimation of Ethyl Alcohol in the Presence of Volatile Substances, especially Aldehyde and Acetone, and the Simultaneous Estimation of the Latter. KARL HOEPNER (*Zeitsch. Nahr. Genussm.*, 1917, **34**, 453—466).—The following procedure is recommended for the estimation of ethyl alcohol, acetaldehyde, and acetone in a mixture of the same in aqueous solution. Ethyl alcohol and acetaldehyde are oxidised to acetic acid by means of chromic acid and sulphuric acid; the unchanged acetone is then distilled and converted into the ketoxime by treatment with hydroxylamine hydrochloride; an equivalent quantity of hydrochloric acid is liberated in the reaction, and its titration gives the amount of acetone present. Acetaldehyde and acetone are then converted into the aldoxime and ketoxime by similarly treating a quantity of the original solution with hydroxylamine hydrochloride; the difference between the quantity of hydrochloric acid liberated in this and in the previous experiment is a measure of the aldehyde present. Ethyl alcohol and acetaldehyde are then estimated together by oxidation with chromic acid. [See, further, *J. Soc. Chem. Ind.*, 1919, 735A.] W. P. S.

Titration of Sugars. E. RUPP and F. LEHMANN (*Zeitsch. Nahr. Genussm.*, 1919, **37**, 162—164).—Further experience confirms the trustworthiness of the method described previously by the authors (*A.*, 1909, ii, 442). If desired, the sugar solution may be mixed with the cold Fehling's solution and water, and the mixture then boiled, etc., as described. (Compare also Frerichs and Mannheim, *A.*, 1917, ii, 393.) W. P. S.

Influence of Acetone on Bang's Method of 1914 for the Estimation of Sugar. N. O. ENGFELDT (*Svensk Farm. Tidskr.* 1919, **23**, 301—308).—The statement has been made by G. Engstrand that acetone reacts with the iodine in the Bang method for the estimation of sugar in blood and urine, causing an error in the results. The author has made several careful tests, using blood, acetone, and β -hydroxybutyric acid. The titrations were not affected by these two substances, and the results in using this method are trustworthy. CHEMICAL ABSTRACTS.

Estimation of Sugar in Blood. HUGH MACLEAN (*Biochem. J.*, 1919, **13**, 135—147).—Improvements and simplification of the method previously published by the author (*A.*, 1916, i, 613) are described. The greater part of the protein is removed by heating with an acetic acid-sodium sulphate solution, the remainder being removed by a small quantity of dialysed iron. The sugar in an aliquot portion of the protein-free filtrate is estimated by boiling with an alkaline copper solution containing potassium iodide and iodate. Careful regulation of the boiling is necessary to ensure accurate results. The solution containing the cuprous oxide in

suspension is cooled, treated with a slight excess of hydrochloric acid, and the free iodine titrated with sodium thiosulphate. The method yields accurate results with as little as 0.2 c.c. of blood.

J. C. D.

The Picric Acid Method for the Estimation of Sugar in Blood, and a Comparison of this Method with that of Maclean. OWEN LAMBERT VAUGHAN DE WESSELOW (*Biochem. J.*, 1919, **13**, 148—152).—A study of the two methods indicated that the results yielded by Benedict's method were invariably higher than those obtained by Maclean's method (see preceding abstract). The possible causes of the discrepancy were considered, and it was found that the high figures given by the first-named method appear to be chiefly due to the presence of an interfering substance or substances, mainly concentrated in the corpuscles, which reacts with the picric acid solution at an early stage of the heating. The Maclean method is therefore considered to be the more accurate one of the two.

J. C. D.

Lewis-Benedict Method of Estimating Blood Sugar. SERGIUS MORGULIS and H. M. JAHR (*J. Biol. Chem.*, 1919, **39**, 119—123).—The presence of creatinine increases the blood sugar value as determined by the Lewis-Benedict method, particularly in the analysis of pathological bloods when the blood creatinine may be high (compare de Wesselow, preceding abstract).

J. C. D.

The Cuprous Chloride-Iodine Method for Reducing Sugars Simplified. F. M. SCALES (*J. Ind. Eng. Chem.*, 1919, **11**, 747—750. Compare A., 1916, ii, 117; 1917, ii, 276).—Twenty c.c. of modified Benedict's solution (copper sulphate, 16.0 grams; sodium citrate, 150 grams; anhydrous sodium carbonate, 130 grams; sodium hydrogen carbonate, 10 grams per litre) and 10 c.c. of the sugar solution (containing not more than 0.02 gram of dextrose) are mixed, heated gradually so as to boil in five minutes, boiled for a further three minutes, and cooled rapidly. The solution is acidified with 100 c.c. of dilute acetic acid, an excess of iodine solution is added, followed by 25 c.c. of dilute hydrochloric acid, and the excess of iodine is titrated with thiosulphate solution after the lapse of one minute. The thiosulphate solution may be standardised against known amounts of dextrose; the ratio of reducing sugar to thiosulphate is constant.

W. P. S.

Studies in Steam Distillation. The Possibilities and Limitations of Duclaux's Method for the Estimation of Homologous Acids. H. DROOP RICHMOND (*Analyst*, 1919, **44**, 255—274. Compare A., 1917, i, 316).—A series of tables is given recording the author's experimental results and showing the quantity of each acid distilled for each 10% by volume distilled, the tables being divided according to the initial strength of acid. Methods of calculation are discussed, and the application of

Duclaux's method in analysis is described; attention is drawn to its usefulness in estimating volatile acids, the purity of an acid, the quantity of impurity present, etc. W. P. S.

Estimation of β -Hydroxybutyric Acid, Acetoacetic Acid, and Acetone in Blood. DONALD D. VAN SLYKE and REGINALD FITZ (*J. Biol. Chem.*, 1919, **39**, 23).—In the process previously described by these authors (A., 1918, ii, 86) it is necessary that the precipitate should be filtered soon after the period of boiling is ended. J. C. D.

Detection of Formaldehyde and Hexamethylenetetramine in Urine. F. UTZ (*Süddeut. Apoth. Zeit.*, 59, 55—56, 64; from *Chem. Zentr.*, 1919, ii, 820—821).—The author's investigations show that the time within which formaldehyde can be detected in the urine after administration of hexamethylenetetramine varies in an extraordinary degree; generally an hour elapses before the detection is successful. The most suitable methods are those of Lebbin, Salkowski, Jorissen and Judd, Collins and Hanzlik, and, particularly, the phenylhydrazine test described by Arnold and Mentzel. When the amount of formaldehyde is very small or the urine is deeply coloured, the specimen is conveniently treated with phenylhydrazine and potassium ferricyanide and shaken with ether; the ethereal solution is agitated with concentrated hydrochloric acid. The red coloration thereby produced appears in the acid layer after the two liquids have separated.

The main portion of hexamethylenetetramine separates as such in the urine. Mercuric chloride in the presence of 10% of alcohol is a suitable precipitant for hexamethylenetetramine, the mode of operation recommended by Schröter being particularly suitable. Precipitation by bromine water gives a useful qualitative test for the presence of hexamethylenetetramine in urine. Esbach's method cannot be applied to the estimation of albumin in urines which contain hexamethylenetetramine; care is also necessary in testing such urines for sugar. H. W.

Titration of *p*-Aminoazobenzene. F. NEITZEL (*Chem. Zeit.*, 1919, **43**, 472).—Trustworthy results may be obtained by diazotising the substance in acid-alcoholic solution. One gram of the sample is dissolved in 100 c.c. of alcohol and 5 c.c. of hydrochloric acid, D 1.19, and the solution is titrated with standardised nitrite solution; iodide-starch paper is used as an external indicator. W. P. S.

Applicability of Cuprammonium Sulphate for the Acidimetric Estimation of Alkaloids according to E. Falières. HERMANN KUNZ-KRAUSE and RUDOLF RICHTER (*Arch. Pharm.*, 1917, **255**, 507—513).—The method suggested by Falières (A., 1899, ii, 713) for the acidimetric estimation of alkaloids in their pure solutions by means of standard cuprammonium solution yields satisfactory results, although the high value of the ratio between corresponding volumes of *N*/10-sulphuric acid and the cuprammon-

ium solution detracts from its sensitiveness; the latter is indeed far below the sensitiveness of the iodeosin method, which admits of the use of $N/100$ -solutions. The Falières method cannot be applied to the estimation of alkaloids in tinctures, extracts, etc., preliminary separation of the alkaloids being necessary if it is to be employed. [See *J. Soc. Chem. Ind.*, 1919, 737A.] T. H. P.

Estimation of Caffeine in Vegetable Material. FREDERICK B. POWER and VICTOR K. CHESNUT (*J. Amer. Chem. Soc.*, 1919, **41**, 1298—1306).—The process for estimating caffeine in tea, described in Allen's "Commercial Organic Analysis," has been considerably modified so as to make it suitable for the analysis of vegetable material generally. The new method is as follows. Ten grams of the finely ground material are extracted for about eight hours with hot alcohol, the extract is added to a suspension of 10 grams of heavy magnesium oxide in 100 c.c. of water, and the whole slowly evaporated nearly to dryness, with frequent stirring. The powder is transferred to a smooth filter and washed with hot water until about 250 c.c. of filtrate collects, when the solution is mixed with 10—20 c.c. of 10% sulphuric acid, and then boiled in a litre flask for about thirty minutes, in order to hydrolyse saponins. The cooled liquid is filtered through a moistened paper into a separating funnel, and shaken with six portions of chloroform of 25 c.c. each. The extracts are decolorised by shaking with 5 c.c. of 1% potassium hydroxide, then run through a dry filter into a conical flask and evaporated, and the caffeine is transferred to a tared beaker and dried in a water-oven. Generally speaking, the residue is nearly white.

Some examples of the application of the method to teas, coffee, coffee leaves and pulp, and guarana are recorded. It is also stated that the "Forest tea" of the Philippines, *Ehretia macrophylla*, Wall, the "New Jersey tea," *Ceanothus Americanus*, Linn., and the "wild coffee" of Florida, *Psychotria undata*, Jacq., do not contain caffeine. J. C. W.

Estimation of Morphine and Solubility of Morphine in Ammonia. A. HEIDUSCHKA and M. FAUL (*Arch. Pharm.*, 1917, **255**, 441—466).—The solubility of morphine in ammonia solutions is found to be proportional to the concentration of the hydroxyl ions of the solution. From the solubility results, a formula is elaborated for correcting the values given by the method of estimating morphine in opium based on the precipitation of the base by ammonia. [See *J. Soc. Chem. Ind.*, 1919, 737A.] T. H. P.

Estimation of Quinine in Urine. BAUR and REVEILLET (*Union pharm.*, 1918; from *Ann. Chim. anal.*, 1919, [ii], **1**, 214—215).—Five c.c. of the filtered urine containing quinine are mixed with 5 c.c. of picric acid solution, and the turbidity obtained is compared with that produced by known amounts of quinine added to normal urine and treated similarly. The method cannot

be applied to urines containing albumin, large quantities of potassium or ammonium salts, or urates. W. P. S.

Specific Colour Reaction of Oxalates. H. CARON and D. RAQUET (*Ann. Chim. anal.*, 1919, [ii], 1, 205).—A reaction described previously (this vol., ii, 351) for the detection of manganese may be used inversely for the detection of oxalates. A red coloration is obtained when an oxalate solution is treated with two drops of 10% manganese sulphate solution, 1 c.c. of acetic acid, and one drop of potassium dichromate solution or a few drops of alkali hypochlorite solution. In the case of an acid solution or of oxalic acid itself, the acetic acid used in the test should be replaced by sodium acetate. The coloration may be obtained with 0.1 gram of oxalic acid; phosphoric acid and hydrofluoric acid do not interfere with the test. W. P. S.

Glucosides with Digitalis-like Action. A New Characteristic Reaction. H. BALJET (*Pharm. Weekblad*, 1918, 55, 457—467).—Digitalin gives a deep red coloration with picric acid and potassium or sodium hydroxide. Gitalin, digitoxin, anhydrogitalin, strophanthin, and *K*-strophanthin give an orange-red coloration with the same reagents. All these glucosides exert an action similar to that of digitalis on the heart. Digitonin, arbutin, amygdalin, and condurangin do not respond to the test. The author suggests that the effect is due to the presence of the carbonyl group linked directly to a carbon atom, such as occurs in the lactone structure of the digitalis glucosides. A positive reaction is also obtained with peptones, probably owing to the presence of creatinine, with acetone, and with aldoses. W. S. M.

A Revised Colorimetric Method for the Estimation of Uric Acid in Urine. OTTO FOLIN and HSIEN WU (*J. Biol. Chem.*, 1919, 38, 459—460).—The method previously described for the estimation of uric acid in blood (Folin and Wu, this vol., ii, 308) may be employed in the analysis of urine. J. C. D.

A Colour Reaction of the Proteins. S. EDLBACHER (*Zeitsch. physiol. Chem.*, 1919, 105, 240—241).—The protein solution is shaken with a solution of sodium hydroxide and methyl sulphate, and, after the decomposition of the latter, concentrated sulphuric acid is added so as to form a layer at the bottom. At the surface of contact of the two layers a reddish-blue colour develops, and, on shaking, the whole liquid assumes this colour.

The coloration resembles that produced in the glyoxylic acid reaction, and, as in that test, is produced by tryptophan. Indole and scatole give a red coloration. The test is regarded as more sensitive than the bromine reaction for free tryptophan.

J. C. D.

The Starch-Iodine Reaction and its Application in the Colorimetric Estimation of Proteins in Immunity Reactions. C. LANGE (*Biochem. Zeitsch.*, 1919, 95, 46—84).—A very full discussion of the reaction of starch with iodine, including a

criticism of Wohlgemuth's method for estimating diastase. The reaction between starch and iodine may be influenced by the presence of other substances, particularly protein, and this fact is made the basis of a method for estimating protein in such fluids as blood, plasma, serum, or bacterial vaccines. The fluids to be compared are treated with a solution of iodine, and, after suitable dilution, are heated for half an hour on the water-bath at 40°. Starch is then added and the colours compared. This process may be used for the standardisation of vaccines.

J. C. D.

Application of Pyramidone in Analysis. ESCHACH (*J. Pharm. Chim.*, 1919, [vii], **20**, 49—52).—Pyramidone in acid solution gives a blue coloration with many oxidising substances (nitrites, ferric chloride, hydrogen peroxide, etc.), but if pyridine is added, a sensitive reagent is obtained for the detection of anæroxydases in blood, raw milk, etc. A blue coloration develops when 1 c.c. of urine containing blood is added to a mixture of 1 c.c. of pyridine, 1 c.c. of pyramidone solution, two drops of hydrogen peroxide, and a few drops of acetic acid. A mixture of pyramidone, dilute copper sulphate solution, and acetic acid gives a blue coloration and a turbidity when treated with a few drops of hydrocyanic acid solution; inversely, this reaction may be used for the detection of copper.

W. P. S.

Methods of Blood Analysis. I. Critical Review of the Methods for Removing Proteins. M. RICHTER-QUITTNER (*Biochem. Zeitsch.*, 1919, **95**, 179—204).—The importance of this phase of blood analysis is emphasised. Removal of proteins by means of precipitation with salts of heavy metals results in low values being obtained for non-protein nitrogen in the filtrate, because the precipitate adsorbs substances such as urea and creatinine. The same drawback applies to the use of colloidal precipitants such as dialysed iron. The removal of proteins by heat is very difficult to carry out satisfactorily.

Of the acid precipitants, the author gives the preference to trichloroacetic acid, but, as in the case of heat precipitation, the values for non-protein nitrogen tend to be high.

A modification of Folin's method for removing protein by methyl alcohol and zinc chlorides is described which gives trustworthy results.

J. C. D.

Precipitation of Proteins by Ammonium Sulphate and Biochemical Reactions. A. CH. HOLLANDE (*Compt. rend. Soc. Biol.*, 1919, 567; from *J. Pharm. Chim.*, 1919, [vii], **20**, 92—94).—Preliminary precipitation of proteins by ammonium sulphate is recommended before precipitin reactions are applied. For instance, urine containing ovalbumin is saturated with ammonium sulphate, the precipitate collected, washed with saturated ammonium sulphate solution, then dissolved in sodium chloride solution, and the albumin identified by precipitin reactions.

W. P. S.

Identification of Pharmaceutical Disulphones, Sulphonal, Trional, and Tetronal. J. A. SANCHEZ (*El Restaurador farm.*, 1918; from *Ann. Chim. anal.*, 1919, [ii], 1, 228—229).—The three substances yield iodoform when treated as follows: A mixture of equal quantities of the sulphone and manganese dioxide is heated in a test-tube, and the vapours evolved are collected in a small quantity of water contained in a second test-tube; the solution thus obtained has an odour of ethyl mercaptan, and when rendered alkaline with sodium hydroxide, heated, and treated with iodine solution, yields iodoform. The three substances may be distinguished from one another by the melting points and by their different solubilities in ether. One gram of sulphonal dissolves in 133 c.c. of ether, 1 gram of trional in 15.57 c.c., and 1 gram of tetronal in 9.83 c.c. W. P. S.

Identification and Assay of Pharmaceutical Disulphones. SCHAMELHOUT (*J. Pharm. Belg.*, 1919; from *Ann. Chim. anal.*, 1919, [ii], 1, 259—260).—Several errors in a recent paper by Sanchez (preceding abstract) are pointed out; sulphonal, trional, and tetronal do not contain a CO group, the ethylsulphonic group does not contain a CH_3 group, and the iodoform reaction is not characteristic of ethylsulphonic groups. W. P. S.

Silver Sodium Salvarsan. I. A. BINZ (*Arbb. aus. Inst. exp. Therapie Georg. Speyer Hause*, 1919, 7, 43—47; from *Chem. Zentr.*, 1919, iv, 37).—Silver is deposited as silver oxide when silver sodium salvarsan is oxidised by hydrogen peroxide in alkaline solution, and the arsenic is converted into a state in which it can readily be detached from the nucleus in the form of arsenic acid, the latter process being advantageously effected with sodium hypochlorite. The method of removing arsenic from organic compounds is not universally applicable in its present form; arsenobenzene gave low results. The analysis of silver sodium salvarsan is performed as follows: The substance (0.6232 gram) is heated to boiling for an hour with water (30 c.c.) and perhydrol (6 c.c.); after addition of concentrated nitric acid (9 c.c.), the solution is evaporated to dryness, when the silver (except for a trace of silver chloride due to the presence of sodium chloride in the preparation) is converted into silver nitrate. The residue is boiled under a reflux condenser for an hour with a solution of sodium hypochlorite (30 c.c.), whereby the silver is completely converted into silver chloride and the arsenic is eliminated. [The hypochlorite solution is prepared by dropping a mixture of water (11 c.c.) and hydrochloric acid (D 1.19; 84 c.c.) on potassium permanganate (13 grams), and absorption of the chlorine in sodium hydroxide solution (10*N*; 60 c.c.) and water (150 c.c.)]. Arsenic is estimated in the filtrate by means of magnesia mixture after decomposition of the excess of hypochlorite with boiling hydrochloric acid, dilution with water, and filtration of silver chloride.

H. W.

General and Physical Chemistry.

Measurements in the Arc Spectrum of Iron for the Purpose of Determining Tertiary Normals. SOPHIE HOELTZENBEIN (*Zeitsch. wiss. Photochem.*, 1917, **16**, 225—251).—Making use of a concave grating, 4 metres radius and 3960 lines per centimetre, the author has re-measured the iron arc spectrum over the range $\lambda\lambda$ 5658—4859 in the third order spectrum, $\lambda\lambda$ 4315—3513 in the fourth order spectrum, and $\lambda\lambda$ 3513—2987 in the fifth order spectrum. Long tables of the wave-length and intensity of the measured lines are given, and an accuracy of about 0.001 Å. is claimed for the values of the wave-lengths. A comparison of the present results with those of Gale and Adams (*Astrophys. J.*, 1912, 35) and St. John and Ware (*ibid.*, 1912, **36**, 14, 203) has been made, and it is shown that very many lines may be used as tertiary normals, and further, that among the lines chosen as tertiary normals very great divergencies are to be observed in the values of the different observers, and consequently more work is necessary before the tertiary normals can be finally chosen. J. F. S.

Series System in the Spectrum of Gold. W. M. HICKS (*Phil. Mag.*, 1919, [vi], **38**, 1—31).—A theoretical discussion of the series systems of the gold spectrum. It is shown that a *D* set corresponding with order $m=1$ exists, which extends far in the ultra-red, and the satellite mantissa of which conforms to the general rule of being a multiple of Δ . Gold, therefore, does not constitute an exception, as formerly appeared to be the case. It is indicated that summation lines for the *P* and *S* series exist. In general, such lines for *S* and *P* will lie far down in the ultra-violet, and this is, no doubt, one reason why they have not been previously recognised. The evidence given in the paper must be supported by further numerical coincidences obtained in other spectra before it is to be regarded as conclusive, but it is sufficient to render it extremely probable. The more accurate determination of the δ depending on $81\delta = \Delta = 113951 - 6p$, where $0.1p$ Ångström is an observational error, has been carried out. This result gives $\delta = 1406.802 - 0.074p$. Taking the ratio of $\delta : (W/100)^2$, where *W* is the atomic weight, to be $361.75 + 0.05q$, the resulting value of the atomic weight of gold is $197.2024 - 0.0052p - 0.0136q$. J. F. S.

The Constitution of the Atom and the Properties of Band Spectra. H. DESLANDRES (*Compt. rend.*, 1919, **169**, 593—599. Compare this vol., ii, 310).—A mathematical discussion in which the author shows that band spectra may be considered as formed by longitudinal and transverse vibrations, the exact part which each plays not being, as yet, fully determined. Two formulæ are deduced which account for the known facts, their

interpretation admitting of longitudinal and transverse vibrations in the atom and molecule, analogous to those in solids. W. G.

The Conditions of Excitation of Fluorescence. L. BRUNINGHAUS (*Compt. rend.*, 1919, **169**, 531—534).—The phenomena of phosphorescence and fluorescence are characterised by the fact that the maximum effect is obtained when the solution is very dilute and the exciting radiation only very feebly absorbed.

W. G.

Photochemical Change in the System $\text{SO}_2\text{Cl}_2 \rightleftharpoons \text{SO}_2 + \text{Cl}_2$ under the Influence of Light Rays of Definite Wave-length. M. LE BLANC, K. ANDRICH, and W. KANGRO (*Zeitsch. Elektrochem.*, 1919, **25**, 229—251).—A long series of experiments are described which are designed to furnish answers to the questions arising from the following case. Given an homogeneous gaseous system, $A + B \rightleftharpoons C$, which is sensitive to light and such that the absorption spectra of A , B , and C respectively do not overlap one another, and which has a zero velocity when in the dark, does the whole system become sensitive to light if it is subjected to light which is absorbed by only one constituent, and, if so, to what extent does the reaction proceed in the direction of C ? The case $\text{SO}_2 + \text{Cl}_2 \rightleftharpoons \text{SO}_2\text{Cl}_2$ has been examined with the object of answering the questions. The absorption spectra of sulphur dioxide, chlorine, and sulphuryl chloride have been determined at a series of pressures, and it is shown that chlorine absorbs all light from the visible region to the middle ultra-violet, and has a maximum at $340 \mu\mu$; sulphur dioxide has an absorption maximum at $290 \mu\mu$ and a minimum at $240 \mu\mu$; sulphuryl chloride vapour absorbs light from $300 \mu\mu$ upwards. Experiments on the decomposition of sulphuryl chloride by light at a series of temperatures, the formation of gaseous sulphuryl chloride, and the formation of liquid sulphuryl chloride are described. It is shown that in the reaction $\text{SO}_2 + \text{Cl}_2 \rightleftharpoons \text{SO}_2\text{Cl}_2$ the formation of secondary products does not occur to the extent of 10%. The illumination of sulphuryl chloride by light, which is practically only absorbed by this substance, brings about quantitative decomposition at both 55° and 100° . The concentration has apparently no influence on the course of the reaction. When the system $\text{SO}_2 + \text{Cl}_2$ is illuminated with light which is absorbed by sulphur dioxide, only a slight reduction of pressure takes place; this is not due to the formation of sulphuryl chloride, but to a side reaction. When the same system is illuminated by light which is only absorbed by chlorine, the formation of sulphuryl chloride takes place until, after a time, a stationary condition is set up. The velocity and also the position of the stationary condition depend, at constant temperature, on the presence of a small quantity of water, and the higher the temperature the earlier the stationary condition is reached. In a number of cases a reversal is noted, so that the stationary condition does not come at the end of diminution of pressure, but of an increase in pressure. At the temperatures 105° and 125° , at which the equili-

brium in the dark is known, the stationary condition lies more to the side of sulphuryl chloride than in the non-illuminated reaction. Under none of the experimental conditions do the two points coincide. The lower the temperature the further apart are the end-points of the illuminated and the non-illuminated reactions. The temperature-coefficient of the formation of sulphuryl chloride from chlorine and sulphur dioxide by light which is only absorbed by chlorine is small, and has little influence on the course of the reaction.

J. F. S.

Photochemical Reactions of Compounds of Less Common Elements. II.

ALFRED BENRATH (*Zeitsch. wiss. Photochem.*, 1917, **16**, 253—261. Compare A., 1915, ii, 504).—An aqueous solution of ammonium molybdate when diluted with an equal volume of either ethyl alcohol or methyl alcohol and exposed to sunlight changes to blue after a short exposure and a reddish-brown substance is deposited on the side of the flask on which the light falls. This compound has the formula $(\text{NH}_4)_2\text{MoO}_4 \cdot 2\text{MoO}_3 \cdot 2\text{MoO}_2 \cdot 6\text{H}_2\text{O}$. In this formation only the complex added group, MoO_3 , and not the neutral ammonium molybdate is reduced. Colloidal molybdic acid is rapidly reduced by alcohol to the blue oxide, Mo_3O_8 . Neutral sodium tungstate is only slowly reduced by alcohol in sunlight, so that after a period of five months' exposure to light only a faint blue colour is produced. On the other hand, suspensions of tungstic acid and acidified solutions of tungstates become deep blue in colour when mixed with alcohol and exposed to sunlight for a few hours. The greenish-yellow powder deposited when uranyl chloride dissolved in ether is exposed to sunlight has been examined and found to have the formula UOCl_2 , and the similar precipitate obtained by exposing an aqueous solution of uranyl nitrate containing a little alcohol to sunlight is $\text{UO}_2(\text{NO}_3)_2$.

J. F. S.

The Relation between Uranium and Radium. VII.

FREDERICK SODDY (*Phil. Mag.*, 1919, [vi], **38**, 483—488. Compare Soddy and Hitchens, A., 1915, ii, 726).—The subsequent growth of radium in the old uranium preparations, since they were last tested in 1915, has confirmed the earlier result that the growth is proceeding according to the square of the time, and that the product of the two periods of average life of ionium and radium is, to an accuracy of some 5%, 237,500,000 years. Assuming the period of radium to be 2375 years, that of ionium is 100,000 years. It is not to be expected that this period will be determined with much greater accuracy, as the result of subsequent measurements upon these preparations.

F. S.

Electrical Conductivity and Other Properties of Saturated Solutions of Copper Sulphate in the Presence of Sulphuric Acid.

H. M. GOODWIN and W. G. HORSH (*Chem. and Met. Eng.*, 1919, **21**, 181—182).—The specific electrical conductance at 25° of saturated solutions of copper sulphate contain-

ing sulphuric acid from 0.15 to 3.6 equivalents per litre has been determined, using the customary Wheatstone bridge arrangement with alternating current. The solutions were rotated in a constant temperature bath and the measurements continued until constant, which indicated saturation. The constant of the conductivity cell was determined by measuring the conductivity of normal potassium chloride solution and a solution of sulphuric acid of maximum conductivity. The results, accurate to 0.5%, show that the conductivity increases, following a straight-line law with increasing concentration of sulphuric acid. The solubility of copper sulphate in the presence of sulphuric acid is determined by electro-analysis. The concentration of copper sulphate at the saturation point falls continuously with increase of concentration of sulphuric acid up to 4 equivalents per litre. The acid content of the solutions was determined by titrating with standard sodium hydroxide solution in the presence of copper sulphate, using methyl-orange as an indicator. The density of the solutions was measured by means of a Mohr-Westphal balance. The density first falls with increasing sulphuric acid content and then increases rectilinearly with a minimum at about 0.5 equivalent per litre. T. H. B.

Applicability of the Precipitated Silver-Silver Chloride Electrode to the Measurement of the Activity of Hydrochloric Acid in Extremely Dilute Solution. G. A. LINHART (*J. Amer. Chem. Soc.*, 1919, **41**, 1175—1180).—Measurements of the *E.M.F.* of cells of the type $\text{Ag}, \text{AgCl} | \text{HCl} | \text{H}_2\text{Pt}$ have been carried out for concentrations of hydrochloric acid varying between 0.04826*N* and 0.000136*N*. The cell was made up in a single vessel, consisting of a bulb of about 1200 c.c. capacity fitted with fairly narrow tubes at the top and bottom. The bottom tube contained the silver-silver chloride electrode, and here a current of hydrogen entered just above the electrode; the top tube contained the hydrogen electrode of iridium coated platinum, and above the electrode was an exit tube for the hydrogen. The silver-silver chloride electrode consisted of a layer of fine-grained electrolytic silver covered with a layer of precipitated silver chloride. After filling, the cell was placed in a thermostat and kept at a temperature of $25^\circ \pm 0.01^\circ$ for three to four days to come to equilibrium, and then the *E.M.F.* measurements were made over a considerable period of time until constant values were obtained. The following values of the *E.M.F.* for a hydrogen pressure of 1 atm. are obtained: HCl, 0.04826*N*, 0.3874 volt; 0.00965*N*, 0.4658 volt; 0.004826*N*, 0.5002 volt; 0.001000*N*, 0.5791 volt; 0.000483*N*, 0.6161 volt; 0.000242*N*, 0.6514 volt; and 0.000136*N*, 0.6805 volt. The *E.M.F.* is calculated to molecular concentration of hydrogen and chloride ions on the assumption of complete ionisation; these values extrapolated at infinite dilution yield the value 0.2234 volt, from which the degree of dissociation is calculated for each dilution. J. F. S.

Transport Number of Chromic Ions in Violet Chloride Solutions. KARL HOPFGARTNER (*Monatsh.*, 1919, **40**, 259—269).—The transport number of the chromic ion in hydrochloric acid solu-

tions of violet chromic chloride has been determined by the Hittorf method. The determinations were effected with solutions of three concentrations (1.00, 0.32, and 0.075 equivalent). The transport numbers found were 0.318 ± 0.005 , 0.357 ± 0.003 , and 0.414 ± 0.005 respectively, which extrapolate to the value 0.446 for the concentration zero, and lineally extrapolate to 0.430. From these values the mobility of the chromic ion is estimated by various methods as 53, 49.5, and 46.3, and of these the first value is probably too high. The results indicate that the chromic ion is surrounded by a fairly large water sheath, although the various methods of calculating the magnitude of this give results which vary considerably.

J. F. S.

Anodic Peroxidation of Manganese in an Acid Medium in Presence of Silver Salts. ARMANDO RUSCONI (*Arch. farm. sper. sci. aff.*, 1919, **27**, 94—96).—When 30% sulphuric acid containing a small proportion (0.05%) of manganous sulphate is electrolysed in a U-shaped voltameter with a potential difference of 5—6 volts, the formation of traces of permanganic acid at the anode is observable after a few minutes. If, however, the solution contains also a few drops of saturated silver sulphate solution, the formation of permanganic acid at the anode is immediate and rapid. Similar results are obtained if the sulphuric acid is replaced by concentrated sodium hydrogen sulphate solution (compare Marshall, A., 1901, ii, 156; Scagliarini and Casali, A., 1913, ii, 181).

T. H. P.

Flowing Metal Vapour Arcs. EMIL PODSZUS (*Zeitsch. Elektrochem.*, 1917, **23**, 179—181).—A metallic vapour arc is described which will burn steadily and continuously in any atmosphere. The lamp consists of a large globe of glass or quartz open at the bottom and fitted with a narrow exit tube at the top. The wide opening at the bottom stands in an iron dish containing mercury, and through the bottom of which are three openings. A narrow glass tube for admitting gas passes through the first; the second opening admits the cathode vessel, and the third the anode vessel. The cathode vessel is made of iron, and down the middle of it a tube of boron nitride passes; covering the top of the cathode is a plate of tungsten perforated by a narrow opening in the centre. The object of the boron nitride tube and the tungsten plate is to stabilise the arc and to prevent fluctuations of the mercury or amalgam which constitutes the cathode. The anode is a tungsten rod. The arc is struck by lowering the anode until it touches the cathode and then drawing it away. The arc produced is a thin, quiet flame, which is affected in colour by the gases in the globe and by the metal used as cathode. In hydrogen the light is greenish-white; in nitrogen bluish-white. All compound gases introduced into the arc were reduced; thus the solid element was obtained from boron trichloride and titanium tetrachloride, whilst calomel was also produced.

J. F. S.

A New Method for the Rapid Determination of Critical Temperatures. Application to Carbonyl Chloride. L.

HACKSPILL and MATHIEU (*Bull. Soc. chim.*, 1919, **25**, 482—485).—A simple apparatus for the determination of critical temperatures consists of a cylinder of aluminium or copper about 25 cm. long and 5 cm. in diameter wound throughout its entire length with nickel wire, by which it is heated electrically. The liquid to be examined, contained in a thick glass tube, is placed in a hole in the axis of the cylinder, and can be viewed through a longitudinal slit in the cylinder. A second hole parallel to the first is provided for a thermometer. The critical temperature of carbonyl chloride was found to be $183 \pm 0.5^\circ$ with this apparatus.

E. H. R.

The Critical Temperature as a Single Function of the Surface Tension. II. MAURICE PRUD'HOMME (*J. Chim. Phys.*, 1919, **17**, 325—328. Compare this vol., ii, 183). The author deduces, on theoretical grounds, the equation, previously put forward (*loc. cit.*), connecting the surface tension with the critical temperature. The relationship is verified in the case of a number of organic liquids.

J. F. S.

The Equation of State of Ethyl Formate. E. ARIÈS (*Compt. rend.*, 1919, **169**, 602—605).—The equation of state of ethyl formate, like that of ethyl acetate (compare this vol., ii, 360), satisfactorily represents the thermal properties of this fluid, except in so far as concerns the heat of vaporisation and the density of the vapour over a temperature range extending from the critical temperature to 35° below it.

W. G.

Standardisation of the Sulphur Boiling Point. E. F. MUELLER and H. A. BURGESS (*J. Amer. Chem. Soc.*, 1919, **41**, 745—763).—The boiling point of sulphur as a standard temperature has been investigated and the conditions under which it should be determined examined. The suggestion that the reflecting power of the inner surface of a radiation shield may influence the temperature assumed by a resistance thermometer is confirmed. A number of shields, both of glass and porcelain, have been examined, and several satisfactory forms are described. The influence of the type of boiling apparatus on the observed temperature is found to be very small. The presence of 0.05% of arsenic in the sulphur has no effect on the boiling point, but 0.10% raises the boiling point 0.02° , 0.05% of selenium, together with 0.10% of arsenic, raises the boiling point 0.08° , and 0.10% of arsenic and 0.10% of selenium raises the boiling point 0.09° . The boiling point of pure sulphur at 760 mm. pressure is 421.73° . The vapour pressure over the range 700 mm. to 800 mm. has been redetermined, and from these values an equation for calculating the boiling point at various pressures is deduced. This has the form $t = 444.60 + 0.0910(p - 760) - 0.000049(p - 760)^2$. A resumé of the conditions to be observed in determining the boiling point of sulphur for standardisation purposes is appended to the paper.

J. F. S.

Determination of Boiling Points of Solutions. F. G. COTTRELL (*J. Amer. Chem. Soc.*, 1919, **41**, 721—729).—A modified boiling-point apparatus is described for solutions whereby the conditions obtaining in the determination of the boiling point of pure liquids are imitated. In the present method, the Beckmann thermometer is placed in the vapour phase and the bulb coated with a thin film of the boiling liquid. The coating of the bulb with the boiling solution is effected by means of a narrow glass tube, which is placed in the liquid; this tube is funnel-shaped at the bottom and sealed at the top, but with a lateral hole just above the bulb of the thermometer. When the liquid boils, bubbles of vapour pass up the tube and carry boiling liquid into a cup through a loosely fitting opening in which the stem of the thermometer passes, the liquid flows over the bulb, and slowly drips back into the solution. It is claimed that this arrangement entirely removes errors due to superheating and yields accurate results extremely readily. J. F. S.

Laws of Concentrated Solutions. VI. The General Boiling-point Law. EDWARD W. WASHBURN and JOHN W. READ (*J. Amer. Chem. Soc.*, 1919, **41**, 729—741).—The boiling points of concentrated solutions of naphthalene and diphenyl in benzene have been determined by means of the Cottrell boiling-point apparatus (preceding abstract). In the determinations, two pieces of apparatus were used, in one of which the pure solvent was kept continually boiling, and in the other the solution, so that the elevation of the boiling point was read directly and was independent of slight pressure changes. The apparatus was further modified by the addition of a side-tube, from which quantities of the solution were extracted for analysis. In the present case, the analysis consisted in determining the density of the solution at 25° and calculating the composition by means of an empirical equation connecting density and composition. The boiling-point law for ideal solutions and the connexion between the boiling-point elevation and the barometric pressure are considered. It is also shown how the molecular weight of a dissolved substance which undergoes solvation may be calculated from the elevation of the boiling point. J. F. S.

Molecular-weight Determination by Direct Measurement of the Lowering of the Vapour Pressure of Solutions. ROBERT WRIGHT (*T.*, 1919, **115**, 1165—1168).

The Evaporation of Concentrated and Saturated Solutions of Ammonium Nitrate, Vapour Pressures, Heats of Solution, and Hydrolysis. E. B. R. PRIDEAUX and R. M. CAVEN (*J. Soc. Chem. Ind.*, 1919, **38**, 353—355r).—The vapour pressures of 47·8%, 60·4%, and saturated solutions of ammonium nitrate have been measured between 40° and 100°. In 60·4% solutions, which are about saturated at the ordinary temperature, the pressure still rises rapidly with rise of temperature, but the

pressures of saturated solutions are low, being no more than 17 cm. at 100°. The heats of evaporation, calculated from the vapour pressures, are, in the case of unsaturated solutions, about 50 cal. lower than that of water at the same temperature, and appear to reach a maximum at some temperature between 60° and 70°. The maximum is more pronounced with saturated solutions, occurring at about 60° with a latent heat of 400 to 450 cal.

When ammonium nitrate solutions are evaporated in contact with iron, there is considerable loss of ammonia and corrosion of the iron by the hydrolytic nitric acid. In acid-resisting vessels or vessels of aluminium, the loss of ammonia through hydrolysis is almost entirely obviated.

E. H. R.

Improved Apparatus for the Estimation of Vapour Pressures. ALLAN MORTON (*J. Soc. Chem. Ind.*, 1919, **38**, 363—364r).—Difficulties having arisen in the determination of the vapour pressures of certain organic liquids on account of the solvent action of these liquids on the lubricants employed for the stopcocks, an apparatus was devised in which taps were entirely avoided. The apparatus took the form of a U-shaped barometer with a bottom mercury reservoir. To the top of each barometer tube was fused a capillary tube, which was bent downwards with its end dipping into a mercury cup. The mercury having been thoroughly cleaned and dried, a sample of the liquid of which the vapour pressure was to be determined was placed in one of the two mercury cups, and, by suitable manipulation of the bottom reservoir, drawn up into one of the arms of the barometer. The difference between the mercury levels in the two arms was a measure, of course, of the vapour pressure.

E. H. R.

The Vapour Pressures of Mixtures of Ether and Sulphuric Acid. ALFRED W. PORTER (*Trans. Faraday Soc.*, 1919, **14**, 280).—A correction to some remarks made by the author in a discussion on a paper by F. H. Campbell (*A.*, 1916, ii, 83).

E. H. R.

Use of Coal as a Substitute for Talcum to Induce Rapid Boiling. E. C. KENDALL (*J. Amer. Chem. Soc.*, 1919, **41**, 1189—1190).—Small, compact pieces of anthracite serve excellently for bringing about rapid boiling of liquids and solutions, and also for preventing the bumping in Kjeldahl flasks. Powdered anthracite has not the same action, and anthracite which has been kept in water for some time loses its efficacy, but after baking for some time the efficacy is regained.

J. F. S.

The Occlusion of Gases by Metals. Introductory Address to General Discussion. SIR ROBERT HADFIELD (*Trans. Faraday Soc.*, 1919, **14**, 173—191).—A historical account of the subject, with special reference to the effect of occluded gases in steel castings. A bibliography is appended.

E. H. R.

General Remarks on Occlusion of Gases in Metals.

ALFRED W. PORTER (*Trans. Faraday Soc.*, 1919, **14**, 192—197).—The term "occlusion" probably covers a number of different phenomena which may take place either singly or in conjunction. These can be enumerated under six heads: first, chemical combination of gas with metal, for example, hydrogen with sodium, potassium, or palladium; secondly, simple solid solution, either separately or in conjunction with the first; thirdly, solid solution in contiguous phases; fourthly, solution accompanied by surface adsorption; fifthly, surface condensation under molecular forces, unaccompanied by solution; sixthly, inclusion, as when large or minute bubbles become entangled in the molten, viscous mass. The work of earlier investigators on occlusion, particularly the occlusion of hydrogen by palladium, is discussed from the point of view of this classification of the phenomena. The influence of condensed gases on the Volta effect is also discussed. E. H. R.

The Physical Properties of Metals as Affected by their Occluded Gases. COSMO JOHNS (*Trans. Faraday Soc.*, 1919, **14**, 198—201).—To explain the profound effect of occluded gases on the physical properties of metals, for instance, the rendering brittle of iron or copper by hydrogen, the following theory is proposed. As a working hypothesis, it is assumed that hydrogen is soluble in the molten metals, but insoluble in the solid, and the theory is adopted that the tenacity of solid metals and the strength of the crystal boundaries are due to the presence of amorphous material, that is, an under-cooled liquid, which serves to cement the crystal grains which compose the solid mass. This intercrystalline matter must contain more hydrogen in solution than the solid metal can hold, and it is therefore at the crystal boundaries that the change in properties occurs, and the brittleness of the whole mass is explained. Relatively small quantities of gas dissolved in the intercrystalline material might thus cause profound changes in the properties of the metal.

The carbon monoxide and carbon dioxide found occluded in steel are probably formed by interaction of dissolved oxide of iron and carbon at the particular temperature when iron oxide, being thrown out of solution as freezing progresses, becomes concentrated in the mother liquor between the growing crystals and reacts with the carbon which has not suffered the same concentration. The gases would thus become concentrated in the intercrystalline layers, and would have the same effect as the hydrogen in copper and iron. Such data as are available on the physical properties of metals or alloys all refer to metals containing unknown quantities of occluded gases, which may profoundly modify their properties, and consequently knowledge of the properties of pure metals, if such can be obtained, is lacking. E. H. R.

Theories of Occlusion: the Sorption of Iodine by Carbon.

J. W. MCBAIN (*Trans. Faraday Soc.*, 1919, **14**, 202—212).—The term "sorption" is employed to include the phenomena of adsorp-

tion, absorption or true solid solution, and chemical reaction, all of which may accompany the fixation of a gas by a solid, and the occlusion of gases by metals is considered as a special instance of the process of sorption. The three processes involved in the phenomenon of sorption differ widely in their time relationships. True adsorption is nearly instantaneous, whilst absorption should obey Fick's diffusion law, commencing with a very high velocity for the first few moments and rapidly falling off with time. Chemical reaction may show the most varied time relationships, since it often proceeds vigorously in surface films as well as in solid solution. Since the occlusion of gases is hastened by rise of temperature, it is reasonable to conclude that the phenomena involved are largely those of diffusion, that is, of absorption rather than adsorption, whilst chemical reaction may play a prominent part.

It was shown by Davis (T., 1907, **91**, 1666) that the sorption by carbon of iodine dissolved in benzene, toluene, and other solvents consists of a surface condensation and a diffusion into the interior. The surface condensation is nearly instantaneous, whilst the diffusion proceeds for weeks or months. After an interval of eleven years, the experiments set up by Davis have been re-examined, and the sorption due to the slow diffusion of the iodine into the charcoal is found to be still continuing. Fresh experiments extending over four years have also confirmed Davis's results. E. H. R.

Balanced Reactions in Steel Manufacture. ANDREW McCANCE (*Trans. Faraday Soc.*, 1919, **14**, 213—223).—A discussion of the equilibrium conditions in the open-hearth furnace during the manufacture of steel. The distribution of ferrous oxide between the steel and the slag and the influence of the furnace gases are particularly considered. E. H. R.

A Few Suggestions on the Theories of Occlusion of Gases by Metals. J. H. ANDREW (*Trans. Faraday Soc.*, 1919, **14**, 232—239).—From a consideration of the experimental evidence available, it is concluded that the occlusion of hydrogen by palladium is dependent on the presence of the active, amorphous form of the metal. Palladium in the crystalline state, free from contamination by the amorphous phase, is inactive towards hydrogen in the cold, but can be rendered active by continually pumping in and extracting gas from the metal, this treatment giving rise to the amorphous form. An amorphous layer of the metal will act as a vehicle for conveying the gas into the crystalline metal, the adsorbed layer of gas acting as a layer of extreme concentration and exerting the same effect as a high external pressure. In the occlusion of hydrogen by iron, the amorphous phase, in this case the intercrystalline cement, probably plays a prominent part. For instance, when a piece of wrought iron is immersed for some time in a saturated solution of sodium hydroxide at 100°, the mass becomes brittle, because the gas is absorbed

more rapidly in the amorphous intercrystalline layers than by the crystals themselves, and the expansion of these layers forces the crystals apart and weakens their cohesion. After remaining longer in the sodium hydroxide, the iron loses its brittleness, because the hydrogen gradually diffuses into the crystals from the intercrystalline cement. Electrolytic iron, being already saturated with hydrogen, is unaffected by sodium hydroxide. It is concluded that diffusion and occlusion are more or less identical, and can be explained by simple physical laws without reference to chemical combination.

E. H. R.

Solutions. A. REYCHLER (*J. Chim. Phys.*, 1919, **17**, 209—265).—A theoretical paper in which many of the properties of solutions are considered. On the basis of Perrin's value of N , the Avogadro number, it is calculated that the mean kinetic energy of one molecule at 0° is 0.5×10^{-13} ergs, and that the charge e of one electron is 4.2×10^{-10} electrostatic units. An explanation of the mechanism of osmotic pressure is evolved, and a method of interpreting certain anomalies observed in osmotic pressure values is indicated. The author has developed the formulæ for calculating molecular weights from boiling-point elevations and freezing-point depressions on the basis of the vapour pressure formula. The nature of ionisation is considered, and it is shown that the ionic equilibrium is a condition of balance between the disruptive forces of the water and the attractions of the ions for one another, which, being of an electrical character, are never entirely eliminated, since they can act over a distance. A connexion is established between ionisation and an adsorption phenomenon. The reasons for the variation of the index in the dissociation laws of Storch and Noyes are considered.

J. F. S.

Unique Case of a Liquid that Exhibits a Minimum Solubility in an Unstable Region. MARSTON TAYLOR BOGERT and JACOB EHRLICH (*J. Amer. Chem. Soc.*, 1919, **41**, 741—745).—On cooling a clear solution of the monohydrate of 3:5-dimethoxyacetophenetidide in boiling water, there appeared a cloud of minute drops, which disappeared on further cooling, with the formation of a clear solution; from this, on continued cooling, white crystals eventually separated. To ascertain the nature of this behaviour, the solubility of this compound has been determined over the temperature range 21.8 — 173.6° . It is shown that the solubility increases with rise of temperature up to 87.5° , when the solid in contact with the solution melts. The solubility of the liquid hydrate increases more rapidly with further rise of temperature. Below 87.5° , the solubility of the liquid hydrate decreases with falling temperature until a point somewhere between 68.5° and 58.1° is reached, when it again increases. Hence the liquid hydrate has a minimum solubility at about 63° . The following solubilities in molecular percentages are recorded. (1) The solid hydrate: 21.8° , 0.010; 39.4° , 0.020; 57.0° , 0.046; 69.5° , 0.076; 72.8° , 0.091; 77.1° , 0.120; 80.2° , 0.151; 84.2° , 0.203; 86.0° , 0.237;

86.9°, 0.257. (2) The liquid hydrate: 35.6°, 0.301; 45.6°, 0.257; 58.1°, 0.237; 68.5°, 0.237; 84.3°, 0.257; 99.8°, 0.303; 111.1°, 0.361; 118.4°, 0.407; 129.2°, 0.499; 173.6°, 2.041. J. F. S.

Intermediate and Complex Ions. V. The Solubility Product and Activity of the Ions in Bivalent Salts. WILLIAM D. HARKINS and H. M. PAINE (*J. Amer. Chem. Soc.*, 1919, **41**, 1155—1168. Compare A., 1917, ii, 77).—In previous papers (*loc. cit.*) it is shown that salts of tri-ionic and higher types ionise in steps and give, even in 0.1*N*-solutions, a large number of intermediate ions. In the present paper, the ionisation of salts composed of a bivalent cation and anion are considered. For this purpose, the solubility of calcium sulphate in water, and in solutions of copper sulphate, magnesium sulphate, and potassium nitrate, has been determined at 18° and 25°. The equivalent conductivity of various concentrations of the four salts and of the solutions of calcium sulphate in the others has been determined at the same temperatures, as well as the densities. The results show that the solubility relations of calcium sulphate when common ions are added are very similar to those of the higher type salts. This indicates the probability that complex ions, such as $\text{Ca}(\text{SO}_4)_2$ and Ca_2SO_4 are present in the solutions. These complex ions differ from what are usually considered under this title, since they are present to a considerable extent in dilute solutions, so in this sense they are more like intermediate ions. If it is assumed that such complex ions are absent, the solubility product, calculated on this basis, is found to increase with great rapidity as the concentration increases; thus, if the total ion concentration increases from 0.02*N* to 0.10*N*, the solubility product is trebled, so, if only simple ions are present, this activity decreases very rapidly with an increase in concentration. On the other hand, the solubility found for the un-ionised part, on the basis of this assumption, remains much more constant than in the case of uni-univalent salts. The change in the slope of these curves is in the direction which is to be expected if complex ions are present. The percentage concentration of such complexes is much higher in copper sulphate solutions than in magnesium sulphate solutions at the lower concentrations. J. F. S.

Reciprocal Solubility of Mixtures of Water, Alcohol, and Ether. A. BOUTIN and A. SANFOURCHE (*Bull. Soc. chim.*, 1919, [iv], **25**, 458—463).—The solubility of water in ether varies but little with temperature, but that of ether in water falls from 12.2% at -3.3°, the freezing point of water saturated with ether, to 4.0% at 35°. By adding one constituent to mixtures of the other two of known composition at 15° until two layers were just formed or just disappeared, limiting values were obtained for a series of ternary mixtures of varying composition. The results are conveniently plotted on a triangular diagram, each corner representing 100% of one constituent. A curve is obtained dividing the triangle into two zones, the one representing homogeneous and the other

heterogeneous mixtures. By drawing tangents to the curve from the points representing pure ether and pure water, the homogeneous zone is divided into six areas. One of these represents mixtures which cannot be made heterogeneous by addition of one constituent; two represent those which can only be made heterogeneous by addition of ether; two others represent those which can only be made heterogeneous by addition of water; whilst the last area represents mixtures which can be separated into two layers by either water or ether. No homogeneous mixture can be made heterogeneous by addition of alcohol alone. E. H. R.

Crystal Lattices and Bohr's Atom Model. L. VEGARD (*Ber. deut. physikal. Ges.*, 1919, **21**, 383—385).—A short criticism of a paper by Born and Landé (this vol., ii, 188), in which the author states that some of the views expressed in the paper, and others attributed to Sommerfeld (A., 1918, ii, 303) were in reality put forward by him at an earlier date (A., 1918, ii, 93, 94, 144), and in consequence he claims priority. J. F. S.

Crystal Lattices and Bohr's Atom Model. M. BORN and A. LANDÉ (*Ber. deut. physikal. Ges.*, 1918, **21**, 385—387. Compare preceding abstract).—An answer to Vegard's criticism (*loc. cit.*), in which the authors allow the priority claim in some respects, but maintain their own in others. J. F. S.

An Experiment Relating to Atomic Orientation. T. R. MERTON (*Phil. Mag.*, 1919, [vi], **38**, 463—464).—On the two assumptions, first, that the axes at right angles to the planes of the rings of electrons in the atom are orientated in a regular manner in a crystal structure, and, secondly, that the direction of expulsion of α - and β -particles from a radioactive atom is also related in some regular manner to this atomic axis, there should be a difference in the α - and β -activities of different faces of certain crystals of radioactive substances. The α -activities of three different faces of large crystals of uranium nitrate have been tested and found to be the same within the error of measurement, so showing that at least one of the two assumptions is incorrect. It is considered the more probable that the α -rays are shot out of the nucleus without regard to the orientation of the atomic axis. F. S.

Colloid Chemistry and its General and Industrial Applications. Second Report. F. G. DONNAN, W. C. M. LEWIS, E. F. ARMSTRONG, ADRIAN J. BROWN, C. H. DESCH, E. HATSCHEK, H. R. PROCTER, W. RAMSDEN, A. S. SHORTER, H. P. STEVENS, and H. B. STOCKS (*Rep. Brit. Assoc.*, 1918, 1—172).—The present report consists of articles on the following subjects: (i) Peptisation and precipitation (pp. 15), Wilder D. Bancroft; (ii) Emulsions (pp. 5), E. Hatschek; (iii) The Liesegang phenomenon (pp. 5), E. Hatschek; (iv) Electrical endosmose, I. (pp. 14), T. R. Briggs; (v) Electrical endosmose, II. (pp. 14), T. R. Briggs: this article deals with de-watering of peat and clay, electrical tanning, preservation of

timber, manufacture of bricks and electro-therapeutics; (vi) Colloid chemistry in the textile industries (pp. 18), W. Harrison; (vii) Colloids in agricultural phenomena (pp. 12), E. J. Russell; (viii) Sewage purification (pp. 15), E. Ardern; (ix) Colloid problems in dairy chemistry (pp. 22), W. Clayton; (x) Colloid chemistry in physiology (pp. 38), W. M. Bayliss; (xi) Administration of colloids in disease (pp. 18), A. B. Searle.

J. F. S.

Vibration and Syneresis of Silicic Acid Gels. HARRY N. HOLMES, WILFORD E. KAUFMANN, and HENRY O. NICHOLAS (*J. Amer. Chem. Soc.*, 1919, **41**, 1329—1336).—The tones produced by vibrating silicic acid gels have been investigated. Silicic acid gels were made which on tapping in thin-walled glass tubes produced a tone two octaves above middle *C*. Such gels vibrate as rigid solids, but tension is an important factor. That the gels are under considerable tension is shown by their great contraction in vaselined tubes. Contracted gels removed from vaselined tubes have a lower vibration frequency than similar gels adhering to the walls of tubes of equal diameter. Since vibration frequency varies inversely as the diameter of the gel column, tension must exert some influence on pitch. Vibration frequency varies directly as the concentration of silicic acid, increases with excess of mineral acid, and decreases with excess of organic acids. Syneresis (separation of aqueous solutions from highly hydrated gels) increases with increase in concentration of silicic acid, increases with excess of mineral acids, and decreases with excess of organic acids. For acid gels the factors which increase vibration frequency also increase syneresis. Vibration and syneresis are directly related to tension, but basic gels are abnormal in this respect. Syneresis varies directly as the free surface. When gels contract in vaselined tubes far more liquid separates than from equal volumes of gel in plain tubes to which the gel adheres.

J. F. S.

Influence of the Age of Ferric Arsenate on its Peptisation. HARRY N. HOLMES and PAUL H. FALL (*J. Amer. Chem. Soc.*, 1919, **41**, 713—717).—Determinations have been made of the amount of a 5*N*-solution of ferric chloride solution required to peptise 1.32 grams of ferric arsenate of various ages. The arsenate was prepared in bottles by adding 3 c.c. of 5*N*-ferric chloride solution to 17.6 c.c. of *M*/5-disodium arsenate solution and shaking vigorously for three minutes. The samples were then preserved, and after measured intervals were treated with ferric chloride solution and vigorously shaken until, by the trial method, the minimum quantity of ferric chloride required for peptisation was found. The experiments were made with ferric arsenate of ages varying up to fifty-six days. It is shown that the amount of ferric chloride required increases rapidly if the precipitate is allowed to age before peptisation—up to an age of one or two days. After this there is only a very small increase in the amount of ferric chloride needed even if the precipitate is kept a month before peptisation. The explanation of this behaviour is found in a decrease in hydration

of the precipitate—rapid during the first day and slow afterwards; also in the formation of larger aggregates with a consequent decrease in the external surface of the particles. Both influences retard diffusion of a solution of a peptising agent and greatly check the rate of peptisation. A few experiments, using ammonium hydroxide and sodium hydroxide as peptising agent, led to similar results.

J. F. S.

Jellies [formed] by Slow Neutralisation. HARRY N. HOLMES and PAUL H. FALL (*J. Amer. Chem. Soc.*, 1919, **41**, 763—764).—Clear gels of ferric arsenate, peptised by ferric chloride, can be prepared by entirely filling a bottle with the sol, covering the neck with a piece of gold-beaters' skin, and placing in a tube attached to the neck 2 c.c. of *N*-ammonium hydroxide, 2 c.c. of saturated calcium hydroxide solution, or 2 c.c. of sodium acetate solution. The base diffuses through the membrane and neutralises the free acid slowly enough to allow of the formation of a perfect gel structure.

J. F. S.

Calculation of the Equilibrium Constants in the Deacon Process. W. D. TREADWELL (*Zeitsch. Elektrochem.*, 1917, **23**, 177—179).—A theoretical paper, in which, making use of known data and the dissociation constants of water and hydrogen chloride, the author shows that the equilibrium constants of the Deacon process are given by the expression $\log K_p = 6034/T - 6.972$. This expression is trustworthy between 300° and 1800°, and the values are nearly correct at temperatures in the region of the atmospheric temperature.

J. F. S.

Influence of Substitution in the Components on the Equilibrium of Binary Solutions. VII. Binary Solutions Equilibria of α - and β -Naphthylamine respectively with Nitro-derivatives of Benzene. ROBERT KREMANN and GEORG GRASSER (*Monatsh.*, 1916, **37**, 723—753. Compare this vol., ii, 275).—Fusion curves have been produced for the binary systems formed between α - and β -naphthylamine respectively and the three dinitrobenzenes, 2:4-dinitrotoluene, 1:3:5-trinitrobenzene, the three mononitrophenols, and 2:4-dinitrophenol respectively. It is shown that neither α - nor β -naphthylamine forms compounds with *o*-dinitrobenzene or *o*-nitrophenol; β -naphthylamine forms no compounds with 2:4-dinitrotoluene. Equimolecular compounds are formed between α -naphthylamine and *p*-dinitrobenzene (m. p. 81.8°), *m*-dinitrobenzene (m. p. 63.8°), 2:4-dinitrotoluene (m. p. 62°), *m*-nitrophenol (m. p. 56.3°), *p*-nitrophenol (m. p. 68.2°), and 2:4-dinitrophenol (m. p. 104.5°). A compound of unknown and undetermined composition is indicated in the system α -naphthylamine-trinitrobenzene. Equimolecular compounds are formed between β -naphthylamine and *p*-dinitrobenzene (m. p. 91°), *m*-dinitrobenzene (m. p. 53.3°), 1:3:5-trinitrobenzene (m. p. 161°), *m*-nitrophenol (m. p. 63.5°), *p*-nitrophenol (m. p. 81.5°), and 2:4-dinitrophenol (m. p. 72.3°). In the case of the

compounds with the dinitrobenzenes, the range of existence is greater for the compounds with α -naphthylamine than for those with β -naphthylamine.

J. F. S.

Influence of Substitution in the Components on the Equilibrium in Binary Solutions. VIII. ROBERT KREMANN and WILHELM CSANYI (*Monatsh.*, 1916, **37**, 755—760. Compare preceding abstract).—Fusion curves have been produced for the binary systems formed between β -naphthylamine and the three dihydroxybenzenes. It is shown that β -naphthylamine forms equimolecular compounds with resorcinol (m. p. 77.6°) and catechol (m. p. 81.3°). A compound (m. p. 141.7°) is formed between two molecules of β -naphthylamine and one molecule of quinol.

J. F. S.

Influence of Substitution in the Components on the Equilibrium in Binary Solutions. IX. A Comparative Determination of the Degree of Dissociation of some Additive Compounds in the Molten Condition. ROBERT KREMANN and GEORG GRASSER (*Monatsh.*, 1916, **37**, 761—774. Compare preceding abstracts).—The degree of dissociation of the equimolecular compounds, formed by naphthalene, α -naphthylamine, β -naphthylamine, and aniline with various other substances, has been calculated. The calculation was carried out by means of the formula of van Laar, $\alpha_0 = (RT_0^2/Q_0)[x^2(1+x)]/[4(T_0-T)]$, in which T_0 is the melting point of the pure compound, α_0 the degree of dissociation, T is the melting point of a mixture of the compound and its components in a concentration x , and Q_0 is the total heat of fusion which is made up of the real heat of fusion q_0 and the heat of dissociation λ . Q_0 is determined experimentally from the initial direction of the fusion curve of the compound and an indifferent substance by means of the expression $(dT/dx) = -RT_0^2/(q_0 + \alpha\lambda) = -RT_0^2/Q_0$. As indifferent substances, p -nitrotoluene and nitrobenzene were used in the experiments. The following values of α_0 were obtained: naphthalene- m -dinitrobenzene, 0.93; naphthalene- p -dinitrobenzene, 0.87; naphthalene-2:4-dinitrotoluene, 0.86; naphthalene-2:4-dinitrophenol, 0.83; α -naphthylamine- m -dinitrobenzene, 0.53; α -naphthylamine-2:4-dinitrotoluene, 0.58; α -naphthylamine- m -nitrophenol, 0.55; α -naphthylamine- p -nitrophenol, 0.56; α -naphthylamine-2:4-dinitrophenol, 0.28; β -naphthylamine- m -dinitrobenzene, 0.88; β -naphthylamine- m -nitrophenol, 0.55; β -naphthylamine- p -nitrophenol, 0.54; β -naphthylamine-2:4-dinitrotoluene, 0.61; aniline- m -dinitrobenzene, 0.23; aniline-2:4-dinitrotoluene, 0.67; aniline-phenol, 0.44; and aniline- m -cresol, 0.10.

J. F. S.

Influence of Substitution in the Components on the Equilibrium in Binary Solutions. XIX. The Binary Systems of Antipyrine with Phenols and their Derivatives. ROBERT KREMANN and OTFRIED HAAS (*Monatsh.*, 1919, **40**, 155—188. Compare this vol., ii, 275).—By means of melting-point curves, the binary systems, antipyrine and phenolic sub-

stances, have been investigated with the object, as in the previous communications, of ascertaining the influence of substitution on the tendency of organic substances to form molecular compounds. In the present papers, the systems antipyrine with phenol, salicylic acid, α -naphthol, β -naphthol, *o*-nitrophenol, *p*-nitrophenol, *m*-nitrophenol, 2:4-dinitrophenol, pyrogallol, catechol, quinol, and resorcinol have been examined and the fusion curves constructed. It is shown that an equimolecular compound is formed between antipyrine and salicylic acid, phenol, α -naphthol, and β -naphthol respectively. In the case of the nitrophenols, antipyrine, as in other cases, forms no compounds with *o*-nitrophenol, but with *p*-nitrophenol three molecular compounds are formed, namely, two molecules of antipyrine with one molecule of *p*-nitrophenol, and one molecule of antipyrine with one and two molecules, respectively, of *p*-nitrophenol. In the cases of *m*-nitrophenol, pyrogallol, and 2:4-dinitrophenol, only the melting-point curves of the pure components could be observed, owing to the extreme slowness of the crystallisation of the melt lying between them. There is little doubt that in these cases one or more molecular compounds exist, but they could not be obtained. Catechol forms three molecular compounds with antipyrine, one molecule of the phenol to one and two molecules of antipyrine respectively, and two molecules of the phenol to one molecule of antipyrine. In the case of quinol, two compounds are formed, two molecules of antipyrine to one and three molecules, respectively, of quinol. J. F. S.

Influence of Substitution in the Components on the Equilibrium in Binary Solutions. XX. The Binary Systems of Acenaphthene with some Nitro-derivatives of Benzene. ROBERT KREMANN and OTFRIED HAAS (*Monatsh.*, 1919, 40, 189—204. Compare preceding abstract).—Fusion curves have been constructed for the binary systems formed between acenaphthene and the three dinitrobenzenes, 2:4-dinitrotoluene, the three nitrophenols, 2:4-dinitrophenol, and picric acid respectively. The systems acenaphthene-*o*-dinitrobenzene and acenaphthene-*p*-dinitrobenzene form no compounds, but simple eutectics; *m*-dinitrobenzene, on the other hand, forms an equimolecular compound (m. p. $70\cdot1^\circ$). In the case of dinitrotoluene, an equimolecular compound is also formed (m. p. $57\cdot5^\circ$). No compounds are formed between acenaphthene and the three nitrophenols, simple eutectics being formed in each case. An equimolecular compound is formed between 2:4-dinitrophenol and acenaphthene (m. p. 86°), and a similar equimolecular compound is formed between picric acid and acenaphthene (m. p. $151\cdot5^\circ$).

J. F. S.

Influence of Substitution in the Components on the Equilibrium in Binary Solutions. XXI. The Binary Systems of Trimethylcarbinol with Phenols and Amines respectively. ROBERT KREMANN and OTTO WLK (*Monatsh.*, 1919, 40, 205—236. Compare preceding abstract).—Fusion curves have

been constructed for the binary systems trimethylcarbinol and the three dihydroxybenzenes, α -naphthol, β -naphthol, pyrogallol, *p*-toluidine, the three phenylenediamines, α -naphthylamine and β -naphthylamine respectively. It is shown that two compounds are formed between catechol and trimethylcarbinol, namely, between two molecules of catechol and one molecule of the alcohol (m. p. 69.7°), and between two molecules of the alcohol and one molecule of catechol (m. p. 29°). In the case of resorcinol and trimethylcarbinol, two compounds are also formed, an equimolecular compound (m. p. 45.8°) and a compound between two molecules of the alcohol and one molecule of resorcinol (m. p. 47.3°). The volatility of trimethylcarbinol rendered the examination of the fusion curve with quinol incomplete, so that nothing can be said of any compounds which may be formed in this case. Pyrogallol, α -naphthol, and β -naphthol each form a single compound with trimethylcarbinol which melt at 56.2° , 1.0° , and 24° respectively. Trimethylcarbinol forms no compounds, but only simple eutectics with *p*-toluidine, *m*-phenylenediamine, and *p*-phenylenediamine. Two compounds are formed between trimethylcarbinol and β -naphthylamine, namely, a compound between two molecules of the amine and one molecule of the alcohol (m. p. 95.5°), and between one molecule of the amine and two molecules of the alcohol (m. p. 92°). In the case of α -naphthylamine, three compounds are formed, namely, between two molecules of the amine and one molecule of the alcohol (m. p. 29.5°), one molecule of the amine and two molecules of the alcohol (m. p. 24.1°), and between one molecule of the amine and six molecules of the alcohol (m. p. 16.0°).

J. F. S.

Influence of Substitution in the Components on the Equilibrium in Binary Solutions. XXII. The Binary Systems Triphenylcarbinol with Phenols and Amines respectively. ROBERT KREMANN and OTTO WLK (*Monatsh.*, 1919, 40, 237—258. Compare preceding abstracts).—Fusion curves have been constructed for the binary systems triphenylcarbinol and phenol, α -naphthol, β -naphthol, quinol, catechol, resorcinol, *p*-toluidine, α -naphthylamine, and β -naphthylamine respectively. It is shown that phenol, α -naphthol, and β -naphthol form only simple eutectics, and no compounds with triphenylcarbinol. Triphenylcarbinol forms a single compound with two molecules of catechol (m. p. 82.0°) and with two molecules of quinol (m. p. 151.6°). In the case of resorcinol, a reddish-brown substance of high melting point separates from the mixture when the concentration of the mixture lies between 25% and 55% of triphenylcarbinol. This compound has not been further examined and is not a molecular compound. No molecular compounds are formed between triphenylcarbinol and *p*-toluidine, α -naphthylamine and β -naphthylamine, respectively, simple eutectics being formed in each case.

J. F. S.

Interchange of Bases in Permutite. GERTRUD KORNFIELD (*Zeitsch. Elektrochem.*, 1917, **23**, 173—177. Compare A., 1918, ii, 315).—The replacement of sodium in sodium permutite by silver, and the replacement of silver in silver permutite by potassium, barium, and ammonium have been studied. It is found that shaking permutite with solutions of the various salts for twenty minutes is sufficient to complete the interchange. In all cases except the replacement of silver by barium, the concentration of the solution has no effect on the amount of change. The change between sodium permutite and silver is represented by the equation $([Ag_P]/[Na_P])^{1.64} \times (Na_L/Ag_L) = 129$, the indices P and L denoting, respectively, permutite and solution. In the case of silver permutite and ammonium nitrate, the reaction is represented by $(Ag_P/[NH_4]_P)^{1.67} \times ([NH_4]_L/Ag_L) = 37.7$. The replacement of silver by potassium is given by the equation

$$(Ag_P/K_P)^{2.17} \times (K_L/Ag_L) = \text{const.} = 9.9,$$

and the replacement of silver by barium by the formula

$$1.5 = (Ag_P/\sqrt{Ba_P})^{2.8} \times (\sqrt{Ba_L}/Ag_L).$$

The various theories put forward to explain the above-mentioned interchange are discussed in the paper. J. F. S.

Wollastonite (CaO, SiO_2) and Related Solid Solutions in the Ternary System Lime-Magnesia-Silica. J. B. FERGUSON and H. E. MERWIN (*Amer. J. Sci.*, 1919, [iv], **48**, 165—189).—A continuation of work previously published (this vol., ii, 401). In the present paper, the solid phases of the ternary system lime-magnesia-silica are examined. The solid phases were obtained by preparing glasses of the desired composition and crystallising at low temperatures. The solids obtained were heated at various temperatures and the changes noted. The results confirm the earlier work with regard to the wollastonite-diopside solid solutions, namely, that wollastonite will take up a maximum of 17% of diopside to form solid solutions. The existence of solid solutions of pseudowollastonite-diopside containing a maximum of 16% of diopside is confirmed. A new compound, $5CaO, 2MgO, 6SiO_2$, is described. Solid solutions of åkermanite (or perhaps of an unstable compound, $3CaO, MgO, 3SiO_2$) in both wollastonite and pseudowollastonite are shown to exist. The wollastonite solutions extend to a composition containing between 60% and 70% of åkermanite, and the pseudowollastonite solid solutions extend to a composition containing about 23% of the same compound. It is shown that an area exists in which the wollastonite-diopside, wollastonite-åkermanite, and wollastonite- $5CaO, 2MgO, 6SiO_2$ solid solutions are all capable of existence. The decomposition temperatures on this area between the 17% diopside solid solution and the compound $5CaO, 2MgO, 6SiO_2$ pass through a minimum. The compound $5CaO, 2MgO, 6SiO_2$ decomposes at 1365° , and the 17% diopside solid solutions at about 1340° , whilst pure wollastonite undergoes inversion at 1200° .

Further, the inversion temperatures and decomposition temperatures of the solid solutions of silica and the compound $3\text{CaO}, 2\text{SiO}_2$ were studied. The results are discussed generally, and diagrams and models to represent the system are drawn. J. F. S.

Graphic Representation of Systems of the Form $a + b = c$ in Triangular Co-ordinates and a [Method of] Presentation of the Phase Rule. WA. OSTWALD (*Zeitsch. Elektrochem.*, 1919, 25, 251—254).—A mathematical paper in which the representation of systems of the form $a + b = c$ on triangular co-ordinates is considered. The use of such a co-ordination system for the general representation of phase-rule problems is discussed. J. F. S.

Theory of Detonation. R. BECKER (*Zeitsch. Elektrochem.*, 1917, 23, 40—49).—The theory of detonation is developed mathematically, and from the equations deduced the following values are calculated, which are of the same order as the experimentally determined values: for a detonation temperature of 2000° with glyceryl trinitrate, a detonation pressure of 92,500 atms. is set up and the detonation proceeds through the mass with a velocity of 7230 metres per sec.; for 2500° the corresponding figures are 110,500 atm. and 7930 metres per sec. J. F. S.

Development of Atomism. I. M. GIUA (*Gazzetta*, 1919, 49, ii, 1—42).—A historical essay with the headings: Genesis of atomism; precursors of atomism in Greece; doctrine of the elements: Anaxagoras and Empedocles; the atomistic system: Leucippus and Democritus; Plato and Aristotle; atomism of Epicurus; atomistics in the poem of Lucretius; atomistics in the Middle Ages; Arabic atomism. T. H. P.

Harmony of the Atomic Weights. EDUARD SCHMIZ (*Ber., Deut. pharm. Ges.*, 1919, 29, 504—518).—The author calculates numerical relationships between the atomic weights of the elements. These relationships are the same as those which exist between the sides, hypotenuse, and radius of the inscribed circle of an isosceles right-angled triangle, and the radius of the circumscribed circle round the squares erected on the sides of the triangle. The ratios of the named lines are $\sqrt{2}/2 : 1 : (\sqrt{2}-1)/2 : \sqrt{5}/2$. Thus in twelve cases it is shown that the ratio of the atomic weights of pairs of elements in the same group of the periodic system is $\sqrt{5} : \sqrt{2}$; in nine other cases the ratio is $\sqrt{5} : \sqrt{5}-1$. In several cases contiguous elements in the same series exhibit the ratio $\sqrt{5}/2 : (2\sqrt{2}-1)/2$. Other relationships of a similar character are also given. J. F. S.

Law of Multiple Proportions. E. PUXEDDU (*Gazzetta*, 1919, 49, i, 203—208).—The various forms in which the law of multiple proportions is expressed, including the new statement of this law by Balareff (A., 1918, ii, 15), are discussed. It is shown that the law,

usually illustrated by means of the oxides of nitrogen and by a few other inorganic and organic groups of compounds, possesses an intrinsic significance different from that commonly attributed to it, and that the new mode of enunciating it is a necessary consequence of various principles of general chemistry, and does not correspond exactly with the original enunciation.

T. H. P.

Determination of Molecular and Atomic Weights; the Density of Gases under Normal Conditions and Critical Constants. J. J. VAN LAAR (*J. Chim. Phys.*, 1919, **17**, 266—328).

—A critical consideration of the methods of calculating atomic and molecular weights of gases from purely physical data. It is shown that for the majority of gases, on the assumption that $v = \infty$, $a = a_c(e^{a/RT})/(e^{a/RT_c})$ and $b = b_c(e^{a/RT})/(e^{a/RT_c})$, where $a = RT_c$. At $0^\circ R T_0 = 1$ and $a_0 = (a_c)_\infty e^{RT_c - 1}$ and $b_0 = (b_c)_\infty e^{RT_c - 1}$. On reducing a_c and b_c of the volume v_c to the volume $v = \infty$, the values become $(a_c)_\infty = \phi a_c$ and $(b_c)_\infty = \phi b_c$, where ϕ is given by the expression $\phi = 1 + \epsilon T_c$, in which ϵ has a value 54×10^{-5} for substances with a critical temperature below 300° Abs. and 43×10^{-5} for substances with a critical temperature above 300° Abs. This difference may probably be expressed by an expression of the type $\phi = 1 + \epsilon T_c - \epsilon' T_c^2$. The value $\epsilon = 43 \times 10^{-5}$ may, however, always be used, since the value of B_0 is nearly always relatively very small for substances with a critical temperature below 300° absolute, so that this value has little influence on the value of M . The function $e^{a/RT}$ often appears too large for diatomic gases, and in this case it may be retained if $\alpha = \frac{1}{2} RT_c$ is employed. In the majority of cases where the critical temperature is above 300° $B_0 = b_0 - a_0 = (b_c - a_c) \cdot e^{RT_c - 1} \times (1 + 0.00043 T_c)$. In this formula b_c may be calculated from the expression $b_c = RT_c / 8 p_c$, and a_c from $a_c = RT_c \times b_c \times 27/8 : \lambda$, where the correcting factor λ is obtained from the formula $\lambda = 27 / (8\gamma - 1) [\gamma / (\gamma + 1)]^2$ and $2\gamma = 1 + 0.038 \sqrt{T_c}$. In the case of abnormal substances a_c and b_c may not be calculated by the above simple formulæ, but by means of much more complicated formulæ which are developed in the paper. The formulæ put forward are used to calculate the atomic weights of carbon, xenon, nitrogen, helium, hydrogen, neon, argon, and krypton from physical data, and yield values in excellent agreement with the accepted values.

J. F. S.

Single Deflexion Method of Weighing. PAUL H. M.-P. BRINTON (*J. Amer. Chem. Soc.*, 1919, **41**, 1151—1155).—To use this method, the balance is given a permanent overload on the left arm by screwing the adjusting nut on one end of the beam until, when the beam and pans are released, the pointer swings out 3 to 7 divisions to the right. The pan arrests must be so adjusted that there is no lateral vibration of the pans when released, and the method may not be used with balances in which the beam and pans are released by a single operation, such as the turning of a single

milled head or lever. In making a measurement after freeing the beam, the pans are released by a gentle, steady motion, the pointer swings out to the right, and the turning point of the single swing is taken as the zero of the balance. To obtain the weight of any object, it is counterbalanced by weights until on releasing the pans the pointer swings out to the same point. A number of readings made by the author and by students are given to show that exceedingly rapid weighing to within 0.1 mg. is possible by this method.

J. F. S.

Self-acting Mercury Pump. A. STOCK (*Zeitsch. Elektrochem.*, 1917, **23**, 35—40).—A self-acting mercury pump, on the Toepler principle, is described, which permits the collection of the gases pumped off. The movable mercury reservoir is replaced by a strong three-necked bottle into which the foot of the pump enters. The mercury is raised by means of air or carbon dioxide under pressure until the pump is full, then by means of valves actuated by the mercury, the pressure is cut off and the mercury falls again. The pump has the advantage, in addition to the ease of operation, that the mercury does not become contaminated with impurities from rubber connexions between its two main parts.

J. F. S.

Greaseless Valve for Gas Work. A. STOCK (*Zeitsch. Elektrochem.*, 1917, **23**, 33—35).—A modification of the floating valve previously described (A., 1915, ii, 339) is given in the paper. This consists of a pair of narrow tubes ground to fit a constriction in each of two parallel tubes. On raising a mercury reservoir connected with the tubes the valves are raised and close the apparatus. The action is similar to that of the valve in a Toepler pump. Three forms of valve are described which are designed for use in working with gases which have chemical action on the lubricant used with glass taps. These valves are made of a porous material which will allow the passage of gases, but not of mercury, so that when the valve is in contact with mercury no gas may pass. The valves are fitted into the glass parts of apparatus by ground joints. These valves may be used in the production of high vacua, and they exhibit no tendency to absorb gases. They are rather slow in action; thus the pressure in a 1350 c.c. flask filled with air was reduced from 760 mm. to 391 mm. in five minutes, to 189 mm. in fifteen minutes, 73 mm. in thirty minutes, and to 0.0006 mm. in ten hours by means of a mercury pump fitted with a double valve of the type described.

J. F. S.

Gas Washing and Absorption Apparatus. FRITZ FRIEDRICHS (*Zeitsch. angew. Chem.*, 1919, **32**, 252—256).—The author discusses the properties of some thirty different forms of gas-washing and gas-absorption apparatus which have been described since the first Woulfe's bottle was used for the purpose. He considers that only those forms which have a "serpentine" principle ensure complete washing or absorption of a gas under reasonable conditions.

W. P. S.

Simple Distillation and Extraction Apparatus. H. W. VAN URK (*Pharm. Weekblad*, 1919, **56**, 1301—1303).—A description, illustrated by a diagram, of a simple apparatus which may be used alternatively for direct distillation or extraction. W. S. M.

Inorganic Chemistry.

An Electrolytic Hydrogen Generator for the Laboratory.

L. D. WILLIAMS (*J. Soc. Chem. Ind.*, 1919, **38**, 355T).—The cell consists of a filter flask of 250 c.c. capacity fitted with a cork carrying a straight tube 30 cm. long and 1.5 cm. wide. The anode is a strip of lead inside the tube 25 cm. long, the lower end as wide as possible, whilst the remainder is 1 cm. wide. The upper end is soldered to a copper lead which supports the electrode so that its lower end is 1 cm. above the bottom of the tube. The cathode is a strip of lead foil thin enough to pass between the cork and the neck of the flask without causing any leakage. The electrolyte consists of 20% sulphuric acid, and should nearly fill the flask when the exit is open. Such a cell will produce 7 c.c. of hydrogen per ampere per minute. The ideal plant for a small laboratory consists of ten cells run normally at 1 ampere, with a variable resistance, an ammeter, and purifying apparatus. The cell can also be used as a source of oxygen. E. H. R.

Physical Constants of Chlorine under the Action of Light.

A. CAMPETTI (*Nuovo Cim.*, 1919, [vi], **17**, i, 143—158).—Experiment shows that the internal friction and the thermal conductivity of chlorine are not appreciably modified by the light from an arc lamp which has been passed through a dilute solution of copper sulphate to free it from most of the less refrangible radiations. The same is, contrary to the conclusions of Trautz (A., 1912, ii, 746), most probably the case with the thermal capacity, that is, the specific heat at constant volume, of the gas. The value of $\eta \times 10^7$ found for chlorine is 1328 at 15°. The thermal conductivity of chlorine is about 0.8 times that of air. T. H. P.

The Catalytic Oxidation of Ammonia. PAUL PASCAL and EUGÈNE DECARRIÈRE (*Bull. Soc. chim.*, 1919, [iv], **25**, 489—507).—Platinum was used as a catalyst in six different states of subdivision, varying from thin platinum foil cut into pieces and made into balls to platinised anhydrous magnesium sulphate. There is a certain minimum temperature for an appreciable velocity of oxidation varying with the physical state of the catalyst. This minimum temperature increases with the curvature of the surface of the catalyst, but is independent of the duration of contact and

of the concentration of the air-ammonia mixture. In every case there is a certain temperature and concentration range over which the maximum oxidation occurs, the yield diminishing outside these limits and becoming insignificant at 900° . In the case where balls of platinum foil were the catalyst, increasing the oxygen content of the air slightly increased the yield. The ammonia not converted into oxides of nitrogen is almost invariably lost as free nitrogen, but there are three exceptions where some of the ammonia passes through unchanged: (1) when the temperature is only about 320° ; (2) when the alveolar industrial catalyst is used; (3) when the catalyst is a plug of very fine platinum wire or wool. [See, further, *J. Soc. Chem. Ind.*, 1919, November.] W. G.

Effect of Diminution of Pressure on the Fixation of Nitrogen as Nitric Oxide by means of the Electric Arc.

E. BRINER and PH. NAVILLE (*Helv. Chim. Acta*, 1919, **2**, 348—352).—As in the formation of ammonia (compare this vol., ii, 148, 190, 338), the optimum yield of nitric oxide from nitrogen-oxygen mixtures under the influence of the electric arc is given when the nitrogen is in excess, when the pressure is low, and when electrodes of certain metals are employed; iron and nickel behave normally, the optimum yield being then obtained with 50% of oxygen, whilst the displacement of the optimum towards the nitrogen-rich mixtures is most marked with platinum and less so with iridium and copper. The actual increases in the yield produced by lowering the pressure and by using excess of nitrogen are less pronounced than in the case of ammonia, but the dependence of the displacement of the optimum yield on a reaction localised in the neighbourhood of the electrodes is more apparent, and is shown only with short arcs and particularly with parallel electrodes. These results are in accord with Guldberg and Waage's law only if the active masses are represented by the concentrations of active particles, and not by the molecular concentrations of the two elements; such active particles are most probably the neutral atoms liberated by the dissociating action of the arc on the molecules. The favourable result obtained by use of excess of nitrogen is explained by the greater resistance to dissociation exhibited by nitrogen molecules. T. H. P.

Alkali Hypochlorites; Free or Combined Salts. Ed. JUSTIN-MUELLER (*J. Pharm. Chim.*, 1919, [vii], **20**, 113—115).—Reasons and evidence are adduced to show that alkali hypochlorites have the formula X_2OCl_2 or $NaOCl \cdot NaCl$, the constituents in the latter formula being combined to form a single molecule. The similarity between the reactions of calcium hypochlorite and alkali hypochlorite favours the combined salt view, as does also the decomposition of calcium hypochlorite by sodium carbonate: $CaOCl_2 + Na_2CO_3 = Na_2OCl_2 + CaCO_3$. The reaction between a hypochlorite and sulphuric acid would be represented by the equation $Na_2OCl_2 + H_2SO_4 = Na_2SO_4 + Cl_2 + H_2O$, whilst the equation

$\text{NaOCl} + \text{NaCl} + \text{H}_2\text{SO}_4 = \text{Na}_2\text{SO}_4 + \text{Cl}_2 + \text{H}_2\text{O}$ would be representative of the reaction if the hypochlorite consisted of NaOCl .

W. P. S.

New Compound of Lime and Bromine and a Process for its Manufacture. JOHN STANLEY ARTHUR and LEONARD GIBBS KILLBY (Brit. Pat., 131750).—A new bactericidal compound, $\text{CaO} \cdot \text{CaOBr}_2 \cdot \text{H}_2\text{O}$, having properties similar to bleaching powder, but stable up to 100° , is produced by heating at 100° the red compound, $\text{CaOBr}_2 \cdot \text{H}_2\text{O}$, formed by acting on quicklime with bromine and water in the proportion of 100 grams of the former to 41 c.c. of bromine and 36 c.c. of water. During the heating, bromine and water are evolved, and the new compound remains as a pale yellow powder containing about 33% of available bromine. [See also *J. Soc. Chem. Ind.*, 1919, 843A.] G. F. M.

Some Chemically Reactive Alloys. E. A. ASHCROFT (*Trans. Faraday Soc.*, 1919, **14**, 271—277).—Alloys of magnesium and lead containing from 5% to 50% of magnesium and 95% to 50% of lead when exposed to moist air rapidly absorb the whole of the oxygen present. The two metals form the compound Mg_3Pb , and the corresponding alloy, containing 19% of magnesium and 81% of lead, is the most reactive of the series. During the oxidation process, the alloy crumbles to a black powder, a mixture of magnesium hydroxide, $\text{Mg}(\text{OH})_2$, and a hydrate of lead sub-oxide, $\text{Pb}_2(\text{OH})_2$, being formed. These hydrates are stable when heated at 200° . The mixture is unaffected by further exposure to dry air, but in presence of water further oxidation occurs, the lead sub-oxide being oxidised to $\text{Pb}(\text{OH})_2$. With the more reactive alloys, the action takes place in the cold, but with those containing upwards of 35% of magnesium, heat is necessary. The use of these alloys is suggested for removing the last traces of oxygen from gas mixtures, for instance, in the preparation of pure hydrogen for aircraft purposes.

When the alloys are boiled with water, oxidation occurs and free hydrogen is formed. The magnesium is oxidised rapidly, but the formation of lead sub-oxide takes place relatively slowly. When, however, the digestion with water is carried out under pressure at about 150° , the lead is completely oxidised to lead oxide and the theoretical quantity of hydrogen is liberated.

Alloys of magnesium and zinc are far less reactive. In fact, these alloys show greater resistance to oxidation than either magnesium or zinc alone (compare Grube, A., 1905, ii, 320).

E. H. R.

Thorium Lead. O. HÖNIGSCHMID (*Zeitsch. Elektrochem.*, 1917, **23**, 161—165).—After a discussion on the atomic weights and origins of the various lead isotopes, the author describes a series of experiments made to determine the atomic weight of the lead extracted from thorite from Ceylon. The method of analysis is the same as that previously described (A., 1914, ii, 653). Four

determinations were made of the ratio $(\text{Th})\text{-PbCl}_2\text{:2Ag}$ and four determinations of the ratio $\text{Th-(PbCl}_2\text{):2AgCl}$. From the first set of measurements the value 207.77 is obtained, and from the second set the value 207.78. From both sets the mean value 207.77 ± 0.14 is calculated as the atomic weight of lead from this source. The present value is entirely in agreement with the value determined by Soddy (T., 1914, 105, 1402) by an indirect method. Assuming the stability of the two isotopes Ra(G) and Th(E), the author calculates that these two substances are present in the ratio 20:7, or that the lead from thorite consists of 8.9% of uranium-lead and 91.1% of thorium-lead.

J. F. S.

Thallium Selenides. LUIGI ROLLA (*Atti R. Accad. Lincei*, 1919, [v], 28, i, 355—359).—According to both Pélabon (A., 1907, ii, 688) and Murakami (A., 1916, ii, 34), thallium and selenium form three compounds, the former giving to them the formulæ Tl_2Se , TlSe , and Tl_2Se_3 , and the latter Tl_2Se , TlSe , and Tl_2Se_3 . The author's attempts at thermal analysis of this system lead to discordant results, the inapplicability of this method depending on the slowness of the reaction involved or on its inconsiderable heat effect. The more sensitive method, consisting in tracing the variation of the solution tension with change of the composition, has therefore been employed, the results obtained excluding the existence of the third thallium selenide, for which different formulæ were given by Pélabon and Murakami.

T. H. P.

Rare Earths. IX. Atomic Weight of Yttrium. III. H. C. KREMERS and B. S. HOPKINS (*J. Amer. Chem. Soc.*, 1919, 41, 718—721).—The atomic weight of yttrium has been determined by the silver chloride method. The yttrium compound was purified by the sodium nitrite precipitation method (A., 1917, ii, 34), and the product converted into oxalate. The oxalate was ignited in a platinum dish and the oxide dissolved in redistilled nitric acid. The solution was filtered and diluted with 2 litres of "conductivity water" in a Jena flask, and treated with ammonia gas. The precipitated hydroxide was washed by decantation, dissolved in nitric acid, and reprecipitated with oxalic acid. The oxalate was again ignited, and the whole process of purification repeated. The final oxide was moistened with water, and hydrogen chloride passed over until all had dissolved, and, after filtering, the solution was stored in a quartz flask. The method of dehydrating, fusing, and weighing the anhydrous chloride was the same as previously described (*loc. cit.*). The anhydrous yttrium chloride was dissolved in a small quantity of water in a small quartz flask, and the solution transferred to a 5-litre glass bottle, diluted with 2 litres of water, and treated slowly with continuous shaking with the same volume of silver nitrate solution containing the calculated amount of silver nitrate. The bottle and contents were then placed in a shaking machine and shaken for twelve hours. The precipitate was allowed to settle, and the solution tested in a nephelometer for an excess of either chloride or silver ions. Additions of a standard solution

of either silver nitrate or sodium chloride were made until equivalence was obtained, and the solution again shaken for several hours. The whole process was carried out in a dark-room. The precipitation was effected in the above manner because earlier experiments had shown that equilibrium was only slowly attained, and dilute solutions with shaking were important factors in reaching a satisfactory end-point. Experiments were made with seven samples, and from the ratio $3\text{Ag}:\text{YtCl}_3$ the atomic weight of 89.33 was obtained, the extreme values being 89.30 and 89.34.

J. F. S.

Reducing Action of Manganous Oxide. V. MACRI (*Boll. chim. farm.*, 1919, 58, 201—202).—Manganous sulphate completely precipitates the silver from a hot ammoniacal silver nitrate solution. The white precipitate formed by addition of the manganous salt to ammoniacal mercuric nitrate solution turns grey and then brown on boiling, and, after treatment with sulphur dioxide solution or an acidified solution of a sulphite, leaves a heavy, brownish-grey, pulverulent deposit, which is not dissolved by dilute nitric acid, but is readily attacked by the concentrated acid, with formation of nitrous fumes. When an ammoniacal solution of copper and manganous sulphates is boiled, cuprous oxide is precipitated; the supernatant, colourless liquid gradually becomes blue in the air. Addition of ammonia to a solution containing a cobalt and a manganous salt yields a precipitate of manganous hydroxide which gradually becomes brown, not, however, by direct reduction of the cobalt oxide, since the latter first undergoes peroxidation in the air, and then gives up its oxygen to the manganese, especially on shaking. No tests were made with gold or platinum, but the hydroxides of other metals are not oxidised by manganous salts.

T. H. P.

Corrosion of Metals, especially Rusting of Iron. F. GOUDRIAAN (*Chem. Weekblad*, 1919, 16, [40], 1270—1285).—The conditions governing the corrosion of metals, especially the rusting of iron, have been investigated by the author. In pure, air-free water the process is purely electrolytic. When the concentration of the Fe^{++} ions in the solution is 1.2×10^{-6} gram-mols. per litre, action ceases. The addition of oxygen produces a very marked effect; the oxidation of the ions gives rise to a fresh *E.M.F.*, and corrosion will continue unless interrupted by a disturbance of the equilibrium of the metal itself. Carbon dioxide is not essential for corrosion; it plays a secondary part only. Nor are the formation and effect of hydrogen peroxide (Traube. A., 1885, 1105) confirmed. In presence of oxygen, the velocity of corrosion $= K(C_0 - C_1)$, C_0 being the solubility of the oxygen in the electrolyte and C_1 its concentration near the iron. Corrosion is greatest where $C_0 = C_1$, that is, where the metal is in contact both with air and water. In weak salt solutions, no effect is observed. Most electrolytes have a maximum "critical" concentration at which corrosion is greatest, but above this concentration the effect diminishes, and many solutions

have also a "limiting" concentration at which corrosion ceases entirely. Tables are given showing values for various electrolytes. Solutions of sodium carbonate above $\pm 0.1N$ strength, and of sodium hydroxide above $0.02N$, are rust-preventive. Ammonium salts generally are very corrosive. The potential of the metal is a dominating factor; an *E.M.F.* of 0.793 volt was obtained with pure iron, which was slightly altered by compression or cooling, but slowly regained its original value. Impurities in iron, by setting up local *E.M.F.*'s up to 20—90 millivolts, accelerate corrosion. The effect of other metals depends on their comparative potentials. Contact with copper increased corrosion of iron by 25—47%, and with nickel by 14—19%. No definite data are obtainable with most metals, however. The composition of rust varies considerably. The author gives many references to the work of other investigators.

W. J. W.

Constitution of Iron-Chromium Alloys. ERNST JÄNECKE (*Zeitsch. Elektrochem.*, 1917, **23**, 49—55).—The system iron-chromium has been examined by means of fusion curves and by the microscopic study of polished sections of the various alloys. The fusion curves were made in a dynamidon (alumina and clay) furnace fitted with a magnesite crucible and heated electrically. The temperatures were automatically recorded by means of a thermo-element and recorder. Curves were produced for six alloys lying between the limits 10Fe:90Cr and 90Fe:10Cr, and all indicate that the system iron-chromium consists of a single eutectic which can form mixed crystals with either component. The eutectic contains 75% of chromium and melts at 1320° ; the limits over which mixed crystals are formed are 55—85% of chromium. The microscopic investigation shows that the crystalline structure is finer the greater the percentage of chromium. The alloys are all tough, and only in the case of the alloys rich in chromium (above 80%) is it possible to break them on an anvil. The alloys are easily scratched by steel and are easily polished. Nitric acid, even when boiling, is without action, but hot 1:1 sulphuric acid attacks them readily. The present results are at variance with previously published results of Treitschke and Tammann (*A.*, 1907, ii, 958), who regard the system as pseudobinary with a single compound of undetermined composition. The author attributes Treitschke and Tammann's results to the presence of aluminium in the chromium used by them.

J. F. S.

Chromium Azoimide. E. OLIVERI-MANDALÀ (*Gazzetta*, 1919, **49**, ii, 43—46. Compare Curtius and Rissom, *A.*, 1899, ii, 90).—Chromium azoimide may be separated by means of the insoluble *pyridine* compound, $\text{Cr}(\text{N}_3)_3 \cdot 3\text{C}_5\text{H}_5\text{N}$, which forms green, crystalline crusts and explodes violently when heated. When boiled, its concentrated aqueous solution deposits mixtures of basic salts of various compositions, the *basic azoimide*, $\text{OH} \cdot \text{Cr}(\text{N}_3)_2 \cdot 2\text{H}_2\text{O}$, which is far less explosive than the original compound, being isolated. Aqueous solutions containing chromium azoimide exhibit the green colour

peculiar to complex chromium salts, and do not yield a precipitate with ammonia solution; even when the experimental conditions are widely varied, addition of silver nitrate does not cause precipitation of the whole of the nitrogen as silver azoimide. T. H. P.

The Crystallography of Uranyl Nitrate Hexahydrate. E. QUERCIGH (*Riv. min. crist. Ital.*, 1915, **44**, 6—14).—A detailed description is given of the crystals, which varied widely in habit according to the solvent employed in their formation.

CHEMICAL ABSTRACTS.

New Method of Analysis of Platinum Ores and Compositions of Native Platinums from the Urals. LOUIS DUPARC (*Helv. Chim. Acta*, 1919, **2**, 324—337).—The modes of occurrence and processes of extraction of platinum in the Urals, and a new method for analysing platinum ores, are described; a table is also given showing the mean compositions of samples of platinum from the chief centres in the Urals. [See, further, *J. Soc. Chem. Ind.*, 1919, 822A.] T. H. P.

Mineralogical Chemistry.

Oceanic Salt Deposits. WILHELM GRÜNEWALD (*Inaug.-Diss. Erlangen*, 1913, 44 pp.; from *Jahrb. Min.*, 1916, ii, Ref. 255).—The work is a continuation of that of van't Hoff and Meyerhoffer, and deals mainly with accurate determinations of the solubility relations of the various salts found in the salt deposits; 1000 mols. H_2O at 25° dissolve 88 mols. KCl , or 111 mols. NaCl , or 12 mols. K_2SO_4 ; at 83° , 118 mols. NaCl . Magnesium sulphate heptahydrate at 25° , 1000 mols. H_2O contain 55 mols. MgSO_4 . Potassium chloride and carnallite at 25° , 1000 mols. H_2O contain 72.5 mols. MgCl_2 and 11 mols. KCl . Magnesium sulphate heptahydrate and picromerite (schœnite) at 25° , 1000 mols. water contain 58.5 mols. MgSO_4 and 5.5 mols. K_2SO_4 . Potassium sulphate and picromerite at 25° , 1000 mols. H_2O contain 22 mols. MgSO_4 and 16 mols. K_2SO_4 . Sodium chloride and magnesium chloride hexahydrate at 25° , 1000 mols. H_2O contain 103 mols. MgCl_2 and 2.5 mols. NaCl . L. J. S.

An Unlisted Mineral. GEORGE J. HOUGH (*Amer. J. Sci.*, 1919, [iv], 48, 206).—A new silver-copper mineral, found in a pocket at a depth of 1100 feet in the Cocinera Mine at Ramos, in San Luis Potosi, Mexico, is described. The mineral is silver-grey in colour with a metallic lustre and slowly tarnishes to black; its streak is leaden-grey, and hardness 2.5. It has $D\ 6.14$, and is quite homogeneous. Its composition is: copper, 60.58%; silver, 27.54%; iron, 1.55%; and sulphur, 9.65%, which would give as the empirical

formula AgCu_4S . The author suggests the name *cocinerite* for the mineral.

J. F. S.

Exchange of the Bases of Zeolites in Neutral Salt Solutions. ILSE ZOCH (*Chemie der Erde*, 1915, 1, 55 pp., and *Inaug.-Diss.*, Berlin; from *Jahrb. Min.*, 1916, ii, Ref. 266—267).—Various zeolites were shaken in solutions of ammonium chloride. Although the reaction proceeds at first with comparative rapidity, yet equilibrium is only slowly reached. For example, for stilbite in grains of 0.25—0.5 mm. equilibrium is reached after forty to fifty days. Temperature, fineness and quantity of powder, and strength of the solution, all exert an influence. There is an exchange only of the bases, calcium, sodium, and potassium, these being replaced by an equivalent amount of ammonium; alumina and silica do not pass into solution, and the amount of chlorine in the latter remains constant. The substitution is accompanied with a change in the optical characters of the material. Chabazite is most readily acted on, then stilbite, heulandite, and harmotome in the order named, whilst scolezite is scarcely affected. Silver nitrate solution acts readily on stilbite at 50°. Copper chloride solution acts on chabazite, stilbite, and heulandite as shown by a change in the birefringence and the green staining; the latter is removed again when the copper is replaced by ammonium.

L. J. S.

Analytical Chemistry.

New Method of Chemical Analysis. A. W. HULL (*J. Amer. Chem. Soc.*, 1919, **41**, 1168—1175).—A method of analysis based on the use of *X*-rays is described. The method consists in passing a beam of monochromatic *X*-rays through the powdered material contained in a glass tube and photographing the diffraction pattern produced. The apparatus required consists of a Coolidge *X*-ray tube fed by a transformer; in front of the tube a screen of suitable metal is placed which acts as a filter (for a molybdenum tube, a zirconium filter is used). The rays passing through the filter are cut down to a narrow beam by means of two lead slits; this beam then passes through the material under analysis, and a fraction of it is scattered. The material is placed at the centre of a photographic film which is bent over a semi-circular strip of wood or brass. After exposure for an hour the film is developed and the photograph compared with photographs prepared from known substances. Substances with a similar crystal structure yield similar patterns, but the intensity and spacing of the individual bands varies with each substance. Examples are given showing that this method is capable of use for analysing mixtures and also gives an approximate quantitative analysis of simple mixtures. J. F. S.

Electrical Apparatus for Use in Electrometric Titrations.

HOWARD S. ROBERTS (*J. Amer. Chem. Soc.*, 1919, **41**, 1358—1362).—A potentiometer is described for use in electrometric titrations. This instrument does not necessarily give the *E.M.F.* readings in volts, but in arbitrary units, since all that is desired in this type of work is the inflexion point of the *E.M.F.* The instrument consists of a rheostat on which two sliding contacts work. The contacts indicate on scales which are numbered in opposite directions, the one from 0 to 100 and the other from 100 to 200. Thus when the point 100 represents zero potential, readings may be made with a solution which changes the sign of its *E.M.F.* without the use of reversing keys and without introducing a minus sign into the figures. The potentiometer is used with a single dry cell and a high resistance galvanometer. J. F. S.

Anti-reflux Device Applicable to Evolution Methods of Analysis.

P. L. ROBINSON (*Chem. News*, 1919, **119**, 159—161).—The apparatus consists of a liquid trap placed between the reaction flask and the absorption vessel; air is admitted through a vertical tube extending into the liquid, when the pressure in the reaction flask diminishes. A similar apparatus for use in the estimation of sulphur in steel is described. W. P. S.

Colorimetric Scale for the Rapid Estimation of the Free Hydrochloric Acid in Liquids by means of a Solution of Brilliant-green.

MAURICE DELORT and ROCHER (*Compt. rend. Soc. Biol.*, 1918, **81**, 646—649).—Two c.c. of a solution (1:5000) of brilliant-green (tetraethyldiaminotriphenylcarbonyl sulphate) are mixed with 2 c.c. of the liquid under examination, for example, gastric juice, and the free hydrochloric acid is estimated by comparison with a colorimetric scale. The colour changes are, to green (0.005% hydrochloric acid), then to yellowish-green (0.03% hydrochloric acid), and then to a more pronounced yellow tint (0.2% hydrochloric acid). Decolorisation occurs in one to two hours with a 0.1% solution of hydrochloric acid, but no decolorisation occurs with acid at a concentration less than 0.03%. The colorimetric scale is furnished by mixing an unfiltered, aqueous alcoholic solution of methylene-blue (1:100), a filtered, neutral solution of potassium chromate (1:20), an unfiltered, aqueous alcoholic solution of eosin (0.10:100), and water in such proportions as to yield mixtures exhibiting tints corresponding with those produced by 0.025%, 0.05%, 0.075%, 0.10%, 0.15%, and 0.2% solutions of free hydrochloric acid; the mixtures are kept in small, sealed tubes. A solution of brilliant-green in distilled water is used as a control. A solution of brilliant-green becomes more or less turbid when it is mixed with undistilled water. Attempts to reproduce the turbidity in the colorimetric scale by means of soap, tincture of gum benzoin, etc., did not give satisfactory results; there is, however, little difficulty in such cases in comparing the opaque tints with the transparent tints of the colorimetric scale. The comparison of tints should be made rapidly (especially for hydrochloric acid at the

higher concentrations) before decolorisation occurs; comparison is made in diffused light and the tubes of the colorimetric scale should be kept in the dark when not in use. The presence of lactic acid causes little difficulty since the tint which it produces differs (in being nearly turquoise blue) from that due to hydrochloric acid and is much less intense than the latter. The influence of combined hydrochloric acid on the reaction is also practically negligible. This is shown by the concordance between estimations of free hydrochloric acid (in presence of combined hydrochloric acid) by this method and by use of Linossier's reagent and by the fact that a hyperacid gastric juice (after exact neutralisation of free hydrochloric acid) gave only a slight colour change when treated with brilliant-green solution, this change in colour being less intense than that corresponding with the minimum of the scale. This method is especially adapted to use under conditions where the usual laboratory facilities are not available.

CHEMICAL ABSTRACTS.

Estimation of Iodides. PAUL GODFRIN (*Bull. Soc. pharm., Bordeaux*, 1919, 16; from *Ann. Chim. anal.*, 1919, [ii], 1, 295—297).—The method depends on the decomposition of the iodide by potassium dichromate in acid solution, the liberated iodine being titrated with thiosulphate solution. Ten c.c. of a 1% solution of the iodide are treated with 1 c.c. of 10% potassium dichromate solution and 15 drops of hydrochloric acid; 20 c.c. of 10% sodium acetate solution, 50 c.c. of water, and 2 c.c. of starch solution are then added, and the iodine titrated with standardised thiosulphate solution. The method may be applied to the estimation of iodides in urine; the influence of substances which absorb iodine is removed by titrating the sample with iodine before the dichromate is added; the liberation of the iodine in this case is at a maximum in three minutes, and the loss is about 2.5% of the quantity of iodine present. W. P. S.

Estimation of Iodide, Bromide, and Chloride in Presence of Each Other. I. M. KOLTHOFF (*Pharm. Weekblad*, 1919, 56, 1298—1300).—The total halogen content in a mixture of chloride, bromide, and iodide is determined by precipitation with silver nitrate. Iodide alone is determined by the addition of excess of iodate after acidifying with benzoic acid, and titration of the iodine liberated by means of thiosulphate. Iodide and bromide are estimated as follows: 25 c.c. of *N*/10-solution of potassium iodate, 5 c.c. of *N*-sulphuric acid, and 20 c.c. of water are added to the solution, and the halogen liberated is driven off by boiling in a Kjeldahl flask. Potassium iodide is now added and a few c.c. of sulphuric acid. The iodine liberated is titrated with thiosulphate. The chloride present is then determined by difference. W. S. M.

Detection of the Halogens in Mixtures of their Salts. A. J. JONES (*Chem. and Drug.*, 1919, 91, 52—53).—Traces of iodide in a bromide or chloride may be detected by the nitrite-

chloroform test, using acetic acid in the proportion of 1 c.c. to 1 gram of the salt and 10 c.c. of water. To detect traces of bromide in chloride or iodide, the salt solution is boiled with the addition of a small quantity of potassium permanganate and phosphoric acid, and the vapours brought into contact with fluorescein paper, the appearance of a red coloration on the paper denoting the presence of bromine. Traces of chloride in iodide or bromide may be detected by treating the salt with chloroform and a mixture of permanganate and phosphoric acid until all the iodine or bromine has been liberated and removed by the chloroform. The aqueous solution is then decolorised with sulphurous acid, the chloride precipitated as silver chloride, and the latter identified by its complete solubility in ammoniacal silver nitrate solution. [See, further, *J. Soc. Chem. Ind.*, 1919, November.] W. P. S.

Iodometric Estimation of Sulphurous Acid and Sulphites.

I. M. KOLTHOFF (*Pharm. Weekblad*, 1919, 56, 1366—1373).—The accuracy of the iodine method of estimating sulphurous acid has been the subject of much investigation, and there is considerable divergence in the literature on the subject. The author prepared a pure solution of sulphur dioxide, free from sulphate, by washing the gas obtained from copper and sulphuric acid with barium nitrate solution, and dissolving it in air-free water containing 5% of ethyl alcohol, the solution being made *N*/20. When sulphurous acid was added to *N*/10-iodine, and the excess of the latter titrated with sodium thiosulphate, very accurate results were obtained. Titration of the iodine by sulphurous acid from a burette until complete reduction took place was also satisfactory. Addition of sodium carbonate or hydrochloric acid introduced errors of 1·2 to 2·6%, due to oxidation by the air. Inaccurate results are obtained if the iodine is added from a burette to the sulphurous acid, and no improvement is gained by adding mannitol (Ruff and Jeroch, A., 1905, ii, 200), sucrose, or alcohol. Solution of pure sodium sulphite, when added to the iodine, gave accurate results, but errors up to 2·8% arose when the iodine was added to the sulphite solution. Addition of potassium iodide, which acts as a catalyst in oxidation, caused errors up to 3·4%, and with sodium hydrogen carbonate divergencies up to 4% were obtained. The author states that inaccuracies are due to oxidation by the air, and denies the influence or formation of free sulphur in the reaction (Volhard, A., 1888, 192). W. J. W.

Estimation of Sulphates in a Concentrated Electrolyte and the Estimation of Sulphur in Foods. VERNON K. KRIEBLE and AUTREY W. MAGNUM (*J. Amer. Chem. Soc.*, 1919, 41, 1317—1328).—The authors have investigated the sodium peroxide method of estimating sulphur in foods with the double object of preventing firing or explosions during the oxidation and of precipitating completely barium sulphate from the solutions, obtained from the fused material, which have a high concentration

of electrolytes. As the result of a large number of experiments carried out under various conditions, the following method of procedure is recommended: a suitable quantity (2—3 grams) of the material is placed in a nickel crucible of 100 c.c. capacity, mixed with 2—3 c.c. of water, and well stirred with a nickel rod, 5 grams of sodium carbonate are added and well mixed, and then sodium peroxide in small quantities until the whole mass becomes dry and granular. The crucible and contents are carefully heated with a Barthel alcohol lamp until the mixture becomes a brown, homogeneous, fused mass; the mixture is cooled somewhat, and more sodium peroxide added to make a total of 25—26 grams; 3 grams of sodium carbonate are also added and mixed with the peroxide. The crucible is then heated by pointing the flame at a position opposite the level of the contents of the crucible until the first signs of oxidation appear, when the flame is removed and the lid placed in position. After the oxidation is complete, the crucible is heated for a further ten minutes. When the crucible is cool it is placed in 100 c.c. of water and heated until the contents are dissolved, 50 c.c. of concentrated hydrochloric acid are added, and the volume increased to 350 c.c. by the addition of water. The solution is raised to the boiling point and precipitation made with 10 c.c. of 10% barium chloride solution, added by means of a dropper at the rate of 10 c.c. in four minutes. The liquid is kept for forty-eight hours, and then evaporated to dryness, the residue is treated with water, and, after keeping for eighteen hours, the precipitate is collected on a Gooch filter. The results of this method are always high, due to adsorbed material in the precipitate, and should be corrected by an amount which is determined experimentally. The correction is obtained by repeating the estimation with a solution of a known amount of potassium sulphate and finding the amount by which the weight of barium sulphate differs from the theoretical quantity. The difference gives the correction value.

J. F. S.

Acidimetric Estimations in Liquids from Aluminium Sulphate Manufacture. I. BELLUCCI and F. LUCCHESI (*Gazzetta*, 1919, **49**, i, 216—241).—The various methods of estimating free and combined sulphuric acid in acid solutions of aluminium sulphate are discussed.

T. H. P.

Alkalimetric Titrations in Presence of Alumina. I. BELLUCCI and F. LUCCHESI (*Annali chim. Appl.*, 1919, **11**, 199—204).—The literature of the subject is discussed and criticised (see preceding abstract).

T. H. P.

The Micro-estimation of Nitrogen by Direct Nesslerisation, and of Total Solids, in Drop Quantities of Human Blood. AMOS W. PETERS (*J. Biol. Chem.* 1919, **39**, 285—298).—The estimation of total solids is made by evaporating the known weight of blood, previously diluted with 0.5% sodium fluoride solution, on a weighed quantity of pure talc powder at 75°

The method of carrying out the digestion of the blood in the micro-Kjeldahl process is minutely described, the most important point in the management of the digestion relating to the process of heating. The colour comparison in the subsequent nesslerisation is made against a single fixed colour standard prepared from picric acid and ferric ammonium sulphate. The conditions of accuracy have been tested, and the method is regarded as trustworthy.

J. C. D.

Estimation of Ammonia in Blood. OTTO FOLIN (*J. Biol. Chem.*, 1919, **39**, 259—260).—It is pointed out that the method employed by Morgulis and Jahr (this vol., ii, 371) yields unsatisfactory results unless every reagent used, including the permute, is absolutely free from ammonia. A method is given for rendering preparations of metaphosphoric acid free from ammonia. When the purified reagents are employed, the amount of ammonia obtained from protein-free blood filtrates is practically nothing, only a greenish-yellow colour being obtained with Nessler's reagent.

J. C. D.

Volumetric Estimation of Hydroxylamine. WILLIAM C. BRAY, MIRIAM E. SIMPSON, and ANNA A. MACKENZIE (*J. Amer. Chem. Soc.*, 1919, **41**, 1363—1378).—The authors have investigated three methods for the volumetric estimation of hydroxylamine: (1) the reduction of hydroxylamine to an ammonium salt by an excess of a titanous salt in acid solution, (2) the oxidation of hydroxylamine to nitrous oxide by an excess of ferric sulphate in sulphuric acid solution with titration of the ferrous salt produced, by potassium permanganate solution, and (3) the oxidation of hydroxylamine to nitrous oxide by iodine in a solution kept neutral by means of disodium hydrogen phosphate. The first two methods are found to be accurate, but the iodine method is unsatisfactory. In addition to the known positive error in the ferric salt method, which is due to the addition of permanganate while some hydroxylamine or an intermediate product, nitroxyl, is still present, a negative error due to oxygen of the air is found under certain conditions. Both errors are easily avoided, the latter by adding the hydroxylamine slowly to a boiling solution of ferric sulphate. Three sources of error are met with in the iodine method: (1) that due to incomplete reaction, which may be avoided by the addition of disodium hydrogen phosphate, (2) nitrite formation, which occurs under all the conditions investigated and constitutes a positive error, and (3) absorption of oxygen from the air, which constitutes a negative error. An empirical method is described whereby theoretical results can be obtained by the iodine method, but this is shown to be due to a compensation of the last-named two errors. Hydroxylamine is oxidised mainly to nitrate by an excess of hypochlorous acid. Sodium thiosulphate in a solution of disodium hydrogen phosphate can be quantitatively oxidised to sulphate by iodine. The reaction is rapid at 70°.

J. F. S.

Influence of Fluorides on the Oxidimetric Estimation of Nitrous Acid. I. BELLUCCI (*Gazzetta*, 1919, **49**, i, 209—216).

—Lunge's method of estimating nitrous acid by means of permanganate leads to fallacious results if the solution contains also fluorine ions in high concentration. This anomaly is due to the same cause as that observed by Müller and Koppe (A., 1910, ii, 957) in the oxidimetric estimation, also in presence of fluorides, of manganese by Volhard's method, namely, the formation of derivatives of tervalent manganese. In the case of nitrous acid, this inconvenience may be overcome by treating the nitrous acid, in a solution acidified with sulphuric acid, with excess of standard permanganate solution, then adding, after a couple of minutes, potassium iodide solution and estimating the iodine liberated by the excess of permanganate by titration with thiosulphate solution. A blank estimation should also be carried out with the same volume of permanganate as is used to oxidise the nitrous acid.

The case studied by Müller and Koppe is not amenable to this procedure, since addition of the alkaline iodide would there result in liberation of iodine in amount corresponding with the quantity of permanganate initially taken. T. H. P.

Estimation of Citrate-soluble Phosphoric Acid by Petermann's Method. H. NEUBAUER and E. WOLFERTS

(*Landw. Versuchs-Stat.*, 1916, **89**, 197—202).—New methods are described for preparing Petermann's ammoniacal citrate solution and for applying it to the estimation of the citrate-soluble phosphoric acid of dicalcium phosphate ("Methodes suivies dans l'analyse des matieres fertilisantes," Gembloux, 1897). [See *J. Soc. Chem. Ind.*, 1919, 837A.] T. H. P.

Electrolytic Resistance Method of Estimating Carbon in Steel. J. R. CAIN and L. G. MAXWELL (*J. Ind. Eng. Chem.*,

1919, **11**, 852—860).—A rapid method of estimating carbon in steel has been based on the absorption of the carbon dioxide, obtained by direct combustion, in barium hydroxide solution, and measuring the change in the electrolytic resistance of the solution caused by the precipitation of the barium ions. A simple form of absorption apparatus has been devised for this purpose, containing a cell in which the electrodes can be adjusted so as to give a definite cell constant, and Weibel's galvanometer has been found an accurate instrument for measuring the resistance. The combustion is carried out in an electric furnace, and the carbon dioxide is expelled by a current of air (freed from carbon dioxide). A table showing the percentages of carbon corresponding with the resistance and the temperature of barium hydroxide solutions of definite concentrations has been made, and from this a nomographic chart has been constructed whereby the percentages may be read directly with an error of less than 0.005% of carbon. [See further, *J. Soc. Chem. Ind.*, 1919, 773A.] C. A. M.

Detection of Carbon Monoxide in Air. DESGREZ and LABAT (*Acad. med.*, 1919; from *Ann. Chim. anal.*, 1919, [iii], **1**, 294—295).—Strips of filter paper are immersed in 10% palladium

chloride solution and then dried in the dark. If a strip, moistened at one end, is suspended in air containing carbon monoxide, the moistened portion becomes grey, brown, or black within six minutes, whilst the dry portion retains its yellow colour. The depth of the coloration depends on the amount of carbon monoxide present; 1 part in 1300 parts of air yields a distinct grey coloration. If the air also contains hydrogen sulphide, the strip should be suspended in a bottle through which the air, previously passed over lead acetate, is aspirated.

W. P. S.

Estimation of the Reaction of Natural Waters. J. TILLMANS (*Zeitsch. Nahr. Genussm.*, 1919, **38**, 1—16).—The reaction (hydrogen ion concentration) of most natural waters is due to free carbon dioxide and to carbon dioxide combined as hydrogen carbonates, and is conveniently expressed as ten thousandths of a mg. per litre ($=h'$). In neutral waters $h'=1$; all values above 1 indicate an acid reaction and all values under 1 an alkaline reaction. Generally, h' can be calculated with sufficient accuracy by multiplying the mg. of free carbon dioxide per litre by 3 and dividing the result by the number of mg. of carbon dioxide present as hydrogen carbonate per litre of water. The exceptions to this rule are described. In the case of alkaline waters, the alkalinity may be expressed as the reciprocal of h . [See, further, *J. Soc. Chem. Ind.*, 1919, November.]

W. P. S.

Acidosis. XVI. Estimations of Bicarbonate in the Blood Plasma of Different Species by the Titration and Carbon Dioxide Capacity Methods. EDGAR STILLMAN (*J. Biol. Chem.*, 1919, **39**, 261—265).—The methods employed were those described by van Slyke, Stillman, and Cullen (*A.*, 1917, i, 521; this vol., ii, 298), and examinations of plasma from the blood of man, dogs, sheep, rabbits, and chickens were carried out. Results obtained by titration agreed with those by the carbon dioxide capacity method, as a rule, within less than two millimolecular in plasma bicarbonate concentration. The results confirm the conclusion reached in the former paper that the two methods may be used interchangeably for clinical and for many experimental purposes.

J. C. D.

The Estimation of Calcium and Magnesium in Different Saline Solutions. E. CANALS (*Bull. Soc. Chim.*, 1919, [iv], **25**, 90—94).—Experiments in which magnesium ammonium phosphate was precipitated by adding a solution of magnesium sulphate to an ammoniacal solution of sodium phosphate containing ammonium chloride showed that considerable excess of phosphate, ammonia, or ammonium chloride or of all three together may be used without the accuracy of the magnesium estimation being thereby affected. Only in special circumstances can magnesium be estimated as oxide or sulphate. Both these compounds are very hygroscopic, and magnesium sulphate is subject to decomposition at a bright red heat.

E. H. R.

Separation and Estimation of Magnesium in the Presence of Fixed Alkalis. P. NICOLARDOT and F. DANDURAND (*Rev. Met.*, 1919, **16**, 193—199).—The most trustworthy method for the separation of magnesium from alkalis consists of precipitating the magnesium by means of ammonium phosphate; the details of this method are too well known to need description. A large excess of ammonium phosphate should be avoided; the small excess which is necessary may be removed subsequently by treatment with ferric chloride and ammonia, and the alkalis may then be estimated. Separation of the magnesium by means of ammonium carbonate in alcoholic solution, barium hydroxide, calcium hydroxide, ammonium oxalate, or mercuric oxide is untrustworthy. A simple method for the estimation of magnesium when alkalis are not present (for example, in the analysis of metallic magnesium and its alloys) depends on the precipitation of the magnesium as magnesium fluoride-hydrofluoride; the magnesium chloride, in neutral solution, is treated with a slight excess of ammonium fluoride, the mixture is evaporated to a syrup on a water-bath, and the residue ignited. The ignited residue consists of magnesium fluoride. This method cannot be employed when alkali chlorides are present in the solution. W. P. S.

Estimation of Metallic Zinc Content of Zinc Dust. W. F. EDWARDS (*Chem. and Met. Eng.*, 1919, **21**, 192).—Neither the hydrogen-gas method nor the reduction of potassium iodate is on the whole suited to the evaluation of zinc dust, used or unused, in sherardising. The amalgam method is not satisfactory for practical purposes, even if carried out with careful attention to details in parallel estimations under identical conditions. The reduction of ferric sulphate gives inconsistent results, but with crystallised ferric ammonium sulphate satisfactory results are obtained, the time required being approximately fifteen minutes against six to thirty-six hours for the gas method. The method is as follows: 1 gram of zinc dust is put into a 600 c.c. Erlenmeyer flask, together with 50 grams of ferric alum in crystals and 100 c.c. of water, the whole being constantly stirred. As soon as the zinc dust is dissolved, 100 c.c. of 1:10 sulphuric acid are added, and the solution titrated against potassium permanganate. Comparisons of results obtained on new and used zinc dust by the hydrogen-gas method and the ferric alum method are given, and show good agreement.

T. H. B.

Simple Method of Analysing Bearing Metal and Similar Alloys. G. OESTERHELD and P. HONEGGER (*Helv. Chim. Acta*, 1919, **2**, 398—416).—The principles on which the method described is based are as follows. The alloy is dissolved in boiling concentrated sulphuric acid, dissolution being complete in a few minutes even with an alloy rich in lead. The antimony passes quantitatively into solution in the tervalent form and the tin as stannic sulphate. The copper and lead are converted entirely into copper and lead sulphates, subsequent dilution with water resulting in the separa-

tion of crystalline lead sulphate, which is readily removed by filtration through a Gooch crucible. In the filtrate the antimony is titrated directly with potassium bromate, the titrated solution being then reduced and the tin, and afterwards the copper, estimated volumetrically. In presence of tin, antimony, and lead, copper may be estimated in a few minutes by a simplified form of electrometric titration with sodium thiosulphate. [See *J. Soc. Chem. Ind.*, 1919, 824A.] T. H. P.

Estimation of Small Quantities of Mercury in Toxicological Investigations. F. CARRESCIA (*Boll. chim. farm.* 1919, 58, 242—244).—Descriptions are given of the methods applied to the estimation of mercury in two cases of attempted poisoning by addition of mercuric chloride to coffee and to a bronchial remedy. [See *J. Soc. Chem. Ind.*, 1919, November.] T. H. P.

A Sensitive Reaction for Manganous Salts. D. H. WESTER (*Pharm. Weekblad*, 1919, 56, 1289—1290).—The author points out that the potassium oxalate test for manganese salts is less sensitive than the tests with lead peroxide and nitric acid, and with persulphate and silver nitrate, both of which are applicable in presence of considerable quantities of chlorides. The reaction may, however, be used as a sensitive test for oxalate. W. S. M.

Estimation of Manganese in Steel by means of Persulphate in the Presence of Chromium and Tungsten. P. NICOLARDOT and A. LEVI (*Rev. Met.*, 1919, 16, 201—216).—Investigation of the persulphate method showed that the most trustworthy results are obtained under the following conditions. A quantity of 0.2 gram of the steel is dissolved in 10 c.c. of 33% sulphuric acid and 0.5 c.c. of nitric acid; the solution is then cooled, 5 c.c. of saturated silver sulphate solution and 0.5 gram of persulphate are added, the solution is diluted to 50 c.c., heated for three to five minutes in a water-bath, the heating being discontinued when the red coloration appears. The mixture is set aside until cold and then titrated with arsenious acid solution; the latter should contain 0.5 gram of arsenious acid and 2.5 grams of sodium hydrogen carbonate per litre, and be standardised against a steel containing a known amount of manganese. If the titrated mixture is again heated, the manganese is reoxidised (a sufficient quantity of persulphate still remains for this purpose), and the titration may be repeated. If the steel contains a large quantity of chromium and less than 1% of manganese, the amount of the latter should be brought up to about 1% by the addition of manganese, in the form of a standard permanganate solution, after the treatment with persulphate. The following method is recommended in the case of a steel containing chromium, tungsten, and vanadium. A weighed amount of 0.2 gram of the steel is boiled with 25% sulphuric acid and 0.5 c.c. of nitric acid until a precipitate of yellow tungstic acid forms and all black particles disappear; the mixture is cooled, sodium hydroxide is added in quantity sufficient

to dissolve the tungstic acid and precipitate the iron, 3 c.c. of phosphoric acid solution (containing 38% P_2O_5) are added, the mixture again cooled, and slightly acidified with sulphuric acid. If the solution thus obtained is not perfectly clear, the estimation must be recommenced. The solution is then treated with 10 c.c. of saturated silver sulphate solution and 1 to 3 grams of persulphate, heated on a water-bath for three to five minutes, cooled. 0.002 gram of manganese (in the form of potassium permanganate solution) is added, and the solution is titrated with arsenious acid solution. The quantity of manganese added is deducted from the result obtained. The authors do not think it advisable to attempt to estimate the chromium and the manganese in the same portion of the sample. W. P. S.

Estimation of Iron in Iron Ores by means of Permanganate. R. SCHWARZ (*Chem. Zeit.*, 1919, **43**, 499—500).—A reply to Brandt (this vol., ii, 373).—The author maintains that the use of sodium silicate in the titration is trustworthy under the conditions described by himself and Rolfes (this vol., ii, 170). W. P. S.

Electrometric Titrations, with Special Reference to the Estimation of Ferrous and Ferric Iron. J. C. HOSTETTER and H. S. ROBERTS (*J. Amer. Chem. Soc.*, 1919, **41**, 1337—1357).—Experiments are described on the estimation of ferrous iron by titration with potassium dichromate and potassium permanganate in which the end-point of the reaction is obtained from the *E.M.F.* of the solution against a calomel electrode. The work is extended to the estimation of ferric iron by means of stannous chloride and the titration of potassium dichromate with stannous chloride. The electrical apparatus used in the work is that described by Roberts (see this vol., ii, 471). A special "titration head" is used to cover the flasks in which the titration is carried out. This consists of a glass cap with three openings at the top; through the first opening a glass tube from the calomel electrode enters, the second opening admits the tip of the burette, and the third carries a platinised platinum electrode and admits a current of carbon dioxide. Using this method, solutions of potassium dichromate as dilute as 0.0005*N* may be employed. The electrometric method makes it unnecessary to remove the excess of a reducing agent which has been added in the reduction of a ferric salt. Conditions, such as acidity, need not be controlled except within very wide limits, and hydrochloric, sulphuric, or hydrofluoric acid may be used. The sensitiveness and accuracy of the method make possible the estimation of a few tenths of a milligram of tin, chromium, ferrous, or ferric iron in the presence of large quantities of some other elements, and its use in the blank estimations involved in some of the ordinary estimations by reducing or oxidising agents. The time within which an estimation can be carried out is greatly shortened. The content of ferrous and ferric iron in a silicate, for example, can be deter-

mined in from fifteen to thirty minutes. The precision attainable is comparable to the best of the ordinary volumetric methods.

J. F. S.

New Method for the Estimation of Chromium. A. TERNI and P. MALAGUTI (*Gazzetta*, 1919, **49**, i, 251—256).—The method previously given for the detection of chromium (A., 1913, ii, 881) is applicable to the estimation of this metal, the procedure being as follows. The solution of the chromic salt is boiled with 20 c.c. of nitric acid (D 1.4) and about 1 gram of lead dioxide in a covered 200 c.c. beaker until the volume is reduced to a few c.c. The liquid is then diluted with 40—50 c.c. of water, treated with sufficient 25—30% sodium hydroxide solution to redissolve the precipitated lead chromate, heated to incipient boiling, and filtered into a conical litre flask, the residue on the filter being washed five or six times with boiling water rendered slightly alkaline with sodium hydroxide. The filtrate is diluted to 150—200 c.c., sufficient nitric acid (D 1.2) absolutely free from nitrous acid being added to dissolve the lead chromate almost completely, and then a further 25 c.c. of the same acid. The acid liquid is treated with 5—10 c.c. of 10% potassium iodide solution, and the iodide liberated titrated with sodium thiosulphate solution containing about 25 grams per litre, previously standardised, in presence of 25 c.c. of the nitric acid of D 1.2, by means of $N/10$ -potassium dichromate solution. The method gives good results and is not invalidated by the presence of iron, manganese, or aluminium.

T. H. P.

Rapid Method of Estimating Uranium in Carnotite. C. E. SCHOLL (*J. Ind. Eng. Chem.*, 1919, **11**, 842).—The difficulties of separating uranium in the presence of iron, aluminium, and vanadium, which are the principal impurities in carnotite, are obviated by adding an excess of ferric iron to the solution, precipitating the iron, vanadium, and most of the aluminium with sodium carbonate at about 90°, and then precipitating the uranium from the boiling filtrate by means of sodium hydroxide. The precipitate is dissolved in dilute nitric acid, the uranium again precipitated by means of ammonia at 90°, and the precipitate ignited and weighed as uranium oxide, U_3O_8 . [See, further, *J. Soc. Chem. Ind.*, 1919, 778A.]

C. A. M.

Rapid Method for the Estimation of Titanium in Titaniferous Iron Ores. JOHN WADDELL (*Analyst*, 1919, **44**, 307—309).—The ore is fused with sodium peroxide in an iron crucible, the mass dissolved in water and sulphuric acid, tartaric acid is added, and the iron precipitated as sulphide by means of hydrogen sulphide and ammonia. After removal of the iron sulphide, the solution is boiled with the addition of sulphuric acid to expel hydrogen sulphide, and the titanium then precipitated by means of "cupferron" (the ammonium salt of nitrosophenylhydroxylamine), or the titanium may be estimated colorimetrically by

hydrogen peroxide. [See, further, *J. Soc. Chem. Ind.*, 1919, 775A.] W. P. S.

Estimation of Zirconium as Phosphate. P. NICOLARDOT and A. RÉGLADE (*Ann. Chim. anal.*, 1919, [ii], 1, 278—281. Compare this vol., ii, 180).—Zirconium may be precipitated quantitatively from a 10% sulphuric acid solution by means of ammonium phosphate; two hours should elapse before the precipitate is collected. Aluminium, iron, chromium, and nickel do not interfere, but the iron should be reduced to the ferrous condition before the zirconium is precipitated. Titanium must not be present. Bismuth is precipitated as phosphate from an acid solution, but this metal rarely occurs with zirconium. W. P. S.

Modified Method for the Analysis of Mixtures of Ethylene and Acetylene. WILLIAM H. ROSS and HARLAN L. TRUMBULL (*J. Amer. Chem. Soc.*, 1919, 41, 1180—1189).—A method of estimating acetylene in mixtures with ethylene and other singly or doubly linked hydrocarbons, based on observations of Chavastelon (A., 1897, i, 545), is described. When acetylene is passed into an excess of a neutral solution of silver nitrate, the solution becomes acid, on account of the reaction $C_2H_2 + 3AgNO_3 = C_2Ag_2, AgNO_3 + 2HNO_3$. The method described consists in shaking a measured volume of the gaseous mixture with a 5% solution of silver nitrate and determining the acidity by titration with standard sodium hydroxide. The titration is effected as follows: after absorption is completed, sodium hydroxide is added to the solution containing the precipitated silver acetylide until the brown colour of silver oxide appears; the excess of silver is then precipitated with 20% sodium chloride solution, and the excess of free alkali in solution finally estimated by titration with standard hydrochloric acid, using methyl-orange as indicator. The method is rapid, accurate, and simple of manipulation, and has the added advantage of giving accurate results for acetylene in mixtures of ethylene or of a gas of such similar properties as vinyl bromide, which is readily absorbed by bromine, fuming sulphuric acid, and by neutral or ammoniacal silver nitrate. J. F. S.

Analysis of Sulphonyl Chlorides of Aromatic Substances. F. NEITZEL (*Chem. Zeit.*, 1919, 43, 500).—Three grams of the powdered substance are mixed with 10 c.c. of water, and free sulphonic acids and mineral acids are neutralised with sodium hydroxide solution, using phenolphthalein as indicator; an excess of *N*/1-sodium hydroxide solution and 20 c.c. of alcohol are then added, the mixture is heated under a reflux apparatus for fifteen minutes, and the excess of alkali is titrated. The quantity of alkali used for the hydrolysis is a measure of the amount of sulphonyl chloride present. W. P. S.

Detection of Methyl Alcohol. HANS WOLFF (*Chem. Zeit.*, 1919, 43, 555).—The presence of higher alcohols in ethyl alcohol

renders the detection of methyl alcohol in the latter untrustworthy if the method used depends on the oxidation of the methyl alcohol and identification of the resulting formaldehyde; the higher alcohols, on oxidation, yield substances which give the same coloration with the morphine-sulphuric acid reagent as does formaldehyde (compare Salkowski, this vol., ii, 249). If, however, *apomorphine* is used in place of morphine in the test, formaldehyde yields a bluish-violet coloration, whilst the oxidation products of the higher alcohols give a yellow or reddish-brown coloration.

W. P. S.

Estimation of Cyanides, Cyanates, and Bromides Present Together. GIUSEPPE VELARDI (*Boll. chim. farm.*, 1919, 58, 241).—Titration with silver nitrate solution gives, in alkaline solution, the cyanide; in solution neutralised with acetic acid, the bromide, cyanide, and cyanate together; in solution acidified with nitric acid, the cyanide and bromide. [See *J. Soc. Chem. Ind.*, 1919, 815A.]

T. H. P.

A Method of Tissue Analysis: Applied to the Posterior and Anterior Lobes of Cattle Pituitaries. C. G. MACARTHUR (*J. Amer. Chem. Soc.*, 1919, 41, 1225—1240).—A modification of Koch's method of tissue analysis is described in which the amount of material required is usually only 10 grams, but may be as low as 2 grams (compare A., 1910, ii, 78—79). The constituents are separated into three groups, proteins, lipins, and extractives, and many instructive determinations made on aliquot parts of each fraction.

The material is first left for several weeks with alcohol, then heated to the boiling point on a few occasions during several days, and finally filtered through a weighed, paper-lined, perforated crucible into a tared beaker, the residue being rinsed with hot alcohol a few times. The residue is next left overnight with ether, warmed several times, and again filtered, using the same crucible and beaker. It is then finely ground and digested with small volumes of hot water, the extract being filtered through the same crucible into a different beaker, evaporated to about 5 c.c., diluted with alcohol, boiled to coagulate the protein, and filtered into the first beaker. All the residues are then transferred by means of alcohol to the crucible, which is placed in a continuous extractor and digested with 95% alcohol for thirty hours, and with chloroform for ten hours. The residual protein is heated in an oven at 105° to constant weight, and the various extracts evaporated in the tared beaker to give the weight of extractives plus lipins. The dried extract is then made into an emulsion with about 40 c.c. of water, treated with 0.5 c.c. of hydrochloric acid to precipitate lipins, centrifuged, and the clear liquid decanted into a 100 c.c. flask containing 5 c.c. of chloroform, shaken, and the aqueous portion poured off into another centrifuge tube, centrifuged, and the clear solution transferred to a second 100 c.c. flask. The lipin residue is treated in the same way with two smaller portions of dilute hydrochloric acid, and finally dissolved in a mixture of alcohol and

chloroform (10:1) in the first 100 c.c. flask, and the volume made up to the mark. The aqueous solution is also made up to 100 c.c.

The further examination of the three fractions follows the usual methods of biochemical analysis, of which the following is a summary. *Extractives*.—(1) Dry weight, ash, and with this any desired inorganic constituents, such as calcium and magnesium. (2) Total nitrogen, by the Kjeldahl method. (3) Nitrogen as ammonia, by rendering a portion slightly alkaline and aspirating the ammonia into 0.01*N*-acid, after which urease is added to the neutralised liquid and nitrogen as urea estimated. (4) Amino-nitrogen, by Van Slyke's micro-method. (5) Creatine and creatinine, by the picric acid, colorimetric method. (6) Uric acid, by the Folin and Denis colorimetric method (A., 1913, ii, 162, 444). (7) Sugar and other substances which reduce Fehling's solution. (8) Total sulphur and sulphur as sulphates. (9) Total phosphorus and phosphorus as phosphates. *Lipins*.—A portion of the solution is evaporated to dryness, hydrolysed by boiling with dilute hydrochloric acid, and thus differentiated into a lipin residue, which is redissolved in chloroform, and a hydrolysis filtrate. Total nitrogen, sulphur, and phosphorus are estimated in the residue, and the filtrate is examined as follows. (1) Total nitrogen. (2) Amino-nitrogen. (3) Volatile amine nitrogen, and, with the same portion, choline nitrogen. (4) Iodine absorbed, by Hübl's method. (5) Total sulphur. (6) Sugar, by the picric acid method. The original lipin solution is also used for the estimation of phosphorus, nitrogen, sulphur, calcium, the iodine value, and also cholesterol, by Bloor's method (A., 1917, ii, 275). *Proteins*.—Phosphorus, sulphur, calcium, chlorine, and total nitrogen are estimated as usual and then the further differentiation is made by Van Slyke's improved method (A., 1915, ii, 851), the nitrogen being recorded as (1) humin nitrogen, (2) ammonia nitrogen, (3) basic nitrogen, (4) arginine nitrogen, (5) histidine nitrogen, (6) lysine nitrogen, (7) cystine nitrogen, (8) mono-amino-nitrogen, (9) non-amino-nitrogen, and (10) α -amino-nitrogen.

The example of the application of this method which is described, is the analysis of the pituitary lobes. The anterior lobe contains 2.4% more solid matter and 4% more protein than the posterior lobe, but there is a great similarity between the proteins of the two lobes. The posterior lobe is 0.9% richer in lipins, these resembling the lipins of the grey matter of the cortex, and also contains 0.9% more extractives, the excess being largely due to non-phosphate phosphorus, amino-nitrogen, and undetermined nitrogen. Both lobes resemble each other so closely that, in spite of their different origin, it may be assumed that they develop together.

J. C. W

General and Physical Chemistry.

Eykman's Refractometric Investigations in Connexion with the Presentation of the Edition of His Works. A. F. HOLLEMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 1200—1203).—A short account of Eykman's unpublished work on the refractometric measurements of organic compounds given on the occasion of the publication of a collection of his published and unpublished work. J. F. S.

Molecular Refractivity of Cinnamic Acid Derivatives. ERIC WALKER and THOMAS CAMPBELL JAMES (*T.*, 1919, **115**, 1243—1247).

The Line Spectrum of Sodium as Excited by Fluorescence. R. J. STRUTT (*Proc. Roy. Soc.*, 1919, [A], **96**, 272—286).—Bakerian Lecture. An improved sodium vapour lamp is described. This consists of a dumbbell-shaped quartz tube placed vertically. In the lower bulb is a pool of sodium which constitutes the cathode. Electric connexion is made by means of an iron or copper wire. The anode consists of a tungsten rod. The lamp is evacuated by means of a Gaede pump. A concentric ring burner surrounds the base of the cathode bulb, by means of which the sodium is kept at a temperature of 180°. The lamp can be run for short periods by a current of 5—6 amps. on a 200 volt circuit, but for prolonged working a lower current, 2·5 amps., is preferable. The lamp is started by means of an induction coil, the terminals of which are connected to the cathode and the constriction of the lamp tube. Using the light from this lamp, the author has examined the resonance effects of sodium vapour. It is shown that excitation of sodium vapour by the second line of the principal series leads to emission of both 3303 and the *D* lines, and that excitation of the *D* lines leads to the emission of the *D* lines only, with 3303. When *D* light falls on sodium vapour of appropriate density, it is known that an intense surface emission occurs from the front layer, and a weak one from succeeding layers. Analysis by absorption in an independent layer of sodium vapour shows that the superficial emission is more absorbable, and therefore nearer the centre of the *D* lines. The breadth of the *D* lines in superficial resonance has been estimated by interferometer methods. It is found to correspond with the breadth conditioned by the Doppler effect, on the assumption that the luminous centre is the sodium atom. Polarisation could not be detected in the ultra-violet radiation, although in accordance with previous observers it was readily observed in *D* resonance. J. F. S.

The Ultimate Rays in the Arc Spectra of the Elements.

M. A. CATALÁN (*Anal. Fis. Quim.*, 1917, **15**, 487—498, and 1918, **16**, 513—519).—A criticism of the conclusions of Gramont (A., 1907, ii, 517, and A., 1908, ii, 645) regarding the ultimate rays of a spectrum. Contradicting the assertion of Gramont, the author shows that in general the ultimate rays in the arc spectra are those of the greatest intensity. This conclusion is supported by a special study of the arc- and spark-spectra of columbium, zirconium, and titanium.

W. S. M.

The Logarithmic Law connecting Atomic Number and Frequency Differences in Spectral Series.

GLADYS A. ANSLOW (*Physical Rev.*, 1919, **13**, 326—336).—Straight lines are obtained by plotting the logarithms of the atomic numbers against the logarithms of the constant frequency differences occurring in the spectral lines of most of the alternate members of Groups I, II, and III of the periodic table; also for sulphur and selenium. Two systems of four approximately straight lines approaching parallelism result when the family has both doublet and triplet series. Equations derived are of the form $\nu = (N/mnk)^A$, where N is the atomic number, A is a constant depending on the system, n is an integer which is the same for both families in any group, k is a constant, 0.080, and m acquires successive integral values for the ν , $\nu_1 + \nu_2$ and ν_1 equations. Elements of high atomic number should lie above the family line. These results indicate the need of modifying the Bohr-Sommerfeld theory of atomic structure before using it for predicting optical series.

CHEMICAL ABSTRACTS.

The Constitution of the Atom and the Properties of Band Spectra.

H. DESLANDRES (*Compt. rend.*, 1919, **169**, 745—752).—A continuation of the theoretical discussion of this subject (compare this vol., ii, 206, 310, 441) and its application to the band spectra of carbon, nitrogen, and cyanogen. The following explanation of the known facts is given. The nucleus of the atom is a cylinder with circular base, which rotates round its axis, its thickness in the direction of the axis being the same for all atoms, but the diameter of the circular base being variable. The nucleus is the seat of longitudinal vibrations developed in the direction of the axis. The thickness being constant, the fundamental vibration is the same for all the elements, the higher harmonics giving the frequencies of the band maxima in the successive spectra. On the main longitudinal vibration are superposed the vibrations of the rings of electrons in three directions in space. The divisions imposed on the nucleus by the nodal surfaces may explain the variations of the elementary groups and their simplification with increasing frequency.

These vibrations require that the shocks in the direction of the axis are propagated with a velocity notably inferior to that of light. The special substance of the nucleus is supposed to be electrified in its mass, and can be likened to ordinary matter rather than to a vacuum, for the propagation of small displacements.

W. G.

Study of the Stability of some Solutions of Enzymes and Alkaloids by means of Ultraviolet Absorption Spectra. The Particular Cases of Pancreatin and Morphine.

HORACIO DAMIANOVICH and ADOLFO WILLIAMS (*Anales Soc. Cient. Argentina*, 1917, **84**, 79—91).—In order to determine the degree of absorption, Dhere's method was used ("Spectrographic Researches on the Absorption of Ultraviolet Rays by Albuminoids, Proteins, and their Derivatives," Univ. of Fribourg, 1909). Aqueous alkaline solutions of pancreatin yielded spectra indicating a gradual absorption in the extreme ultraviolet, but without any band indicating selective absorption. Compared with Dhere's results a notable difference was observed. Albuminoid substances show an absorption band in the ultraviolet spectrum which for a given concentration and thickness includes radiations between 2927 Å. and 2628 Å., whereas in the given case the band did not appear in a solution of 10:1000 strength and 5—10 mm. thickness. Solutions were submitted to temperatures between 40° and 110° for one-half to forty-eight hours. Some alteration in the absorption was noticeable; the conclusion was reached that temperature influences the action. Substances such as glycerol, peptone, and casein, which protect trypsin or pancreatin against the destructive action of heat, act in a similar way towards causing a variation in the ultraviolet spectrum. A solution of morphine (1:10,000) showed appreciable absorption in the ultraviolet, as did also solutions of theobromine, but no band was observed, although neutral aqueous solutions of the hydrochloride showed a faint band between 2950 Å. and 2767 Å. The addition of sodium carbonate (3% solution) to a solution of morphine hydrochloride (1:1000) produced absorption of the extreme ultraviolet and a clear absorption band which increased somewhat with the temperature. Sodium hydroxide causes a similar displacement.

CHEMICAL ABSTRACTS.

Observations and Measurements on Optically Active Crystals (NaClO_3). ELIGIO PERUCCA (*Nuovo Cim.*, 1919, [vi], **18**, ii, 112—154).—The author describes a new polarimetric arrangement, which he has applied to the measurement of the rotatory power of pure, crystalline sodium chlorate and of crystals of the chlorate coloured with "extra China blue" [probably sodium (or ammonium) triphenyltri-*p*-aminodiphenyltolylcarbinoldi-(or mono-)sulphonate], which exhibits a very sharp absorption band in the green. These coloured crystals are obtained, although not always, by moderately rapid cooling of a hot saturated solution of the chlorate and the colouring matter; ultramicroscopic examination of the crystals shows that the blue dye is not present in them in the colloidal condition.

The results obtained indicate that only as a first approximation can the rotatory power of solid sodium chlorate be regarded as a constant, variations greater than the experimental error being observed with different crystals and also with one and the same crystal in different directions and at different points. The mean value obtained for $[\alpha]_D^{13}$ is $+3.120^\circ$. The rotational dispersion,

which shows no deviations from the curve of normal dispersion greater than the errors of observation, may be expressed for the temperature 13° by the following equation, λ being in $\mu\mu$ and $[\alpha]_\lambda$ in degrees: $[\alpha]_\lambda = 1168300/\lambda^2 - 0.3514 + 0.000000306\lambda^2$; Lowry's formula, $[\alpha]_\lambda = a/(\lambda^2 - b)$ (T., 1913, 103, 1067) is inapplicable in this case.

With the coloured crystals, for the light comprised in the spectral zone absorbed (maximal absorption at about $\lambda = 548 \mu\mu$), the rotatory power is found to vary when the crystal is rotated round the light ray as axis, that is, to vary with the azimuth of the crystal with respect to the incident luminous vibration. The course of this variation is sinoidal, and for $\lambda = 546.1$ the maximum variation amounts to as much as 1° per 3.66° for a thickness of 1 millimetre. With crystals deeply coloured, more marked effects still are observed; thus, in one case, for $\lambda = 589.3 \mu\mu$, the difference between the maximal and minimal rotations per millimetre of thickness reached 1.3° . In no instance, however, was change in the sign of the rotation found. There appears to be no very simple relation between the intensity of the coloration and the extent of the variation in rotation. This phenomenon persists without marked alteration when the crystals are heated to about 85° , but at this temperature it suddenly disappears and does not reappear when the crystals are cooled.

In these artificially coloured sodium chlorate crystals there is, as a rule, co-existence of two tetrahedra, each of which, united to a pentagonal dodecahedron, is characteristic of crystals having rotatory power of a certain sign and of normal magnitude at all points. Groth (*Ann. Phys. Chem.*, 1876, 158, 214) refers to the possibility of the co-existence of two tetrahedra in a single crystal of sodium chlorate, but the author was unable to obtain such a crystal under widely varying conditions of crystallisation. T. H. P.

Precision Measurements in the X-Ray Spectra. II. The X-Ray Spectrum of Tungsten. MANNE SIEGBAHN (*Phil. Mag.*, 1919, [vi], 38, 639—646. Compare this vol., ii, 261).—The *K* and *L* series of X-ray lines have been measured for tungsten by means of a spectrograph built on the same principle as that previously described (*loc. cit.*). The measurements were made with rock-salt ($\log 2d = 0.7503541$) and calcite ($\log 2d = 0.7823347$), and the two sets of results shown to be remarkably close to one another, a fact which speaks for the accuracy of the calcite lattice constant in reference to that of rock-salt. In the *K* series the strongest line, $K\alpha$, has the value $208.85XU$, the α_2 line is determined with reference to the α_1 line and the value $K\alpha_2 = 213.52XU$ obtained. The lines $K\beta_1$ and $K\beta_2$ have the values 184.36 and 179.40 respectively. The values are compared with those of de Broglie, Hull and Rice, Dauvillier, and Dershem, and those of the last-named shown to be most nearly in accord with the author's work. The measurement of the *L* series was carried out with the vacuum spectrograph previously described (*loc. cit.*). The following values were obtained: $L\alpha_1$, 1473.48 ; $L\alpha_2$, 1484.52 ; $L\beta_1$, 1279.17 ; $L\beta_2$, 1241.91 ; and $L\gamma_1$,

1095·53. The fainter lines of this series have been measured with reference to one of the stronger lines, and the following frequency differences obtained: $\epsilon - \eta = l - \eta = 98\cdot76$; $\beta - \alpha' = \beta_1 - \alpha_2 = 98\cdot54$; $\delta - \gamma = \gamma_1 - \beta_2 = 98\cdot05$; $\theta - \xi = \gamma_2 - \beta_5 = 97\cdot55$. These figures confirm to a certain extent Sommerfeld's view that the *L* series can be divided into two groups with constant frequency differences between the lines.

J. F. S.

Precision Measurements in X-Ray Spectra. III. An X-Ray Spectrograph for Medium Wave-lengths. MANNE SIEGBAHN and A. B. LEIDE (*Phil. Mag.*, 1919, [vi], **38**, 647—651. Compare preceding abstract).—An X-ray spectrograph is described which is designed to bridge the regions measured by the instruments described in the previous papers (*loc. cit.*). In the present instrument the slit is placed behind the crystal. The crystal table is in fixed connexion with a high precision circle scale which can be turned in relation to the slit and plate-holder. To fix the crystal in the required position and for micrometrical adjustments, the circle is provided with a tangent screw attached to the arm for the plate-holder. Crystal table and plate-holder as a whole can be turned about the same axis. A circle scale and nonius on the back of the spectrograph serve to give an approximate adjustment of the crystal to receive the X-ray pencil under the reflexion angle required. The plate-holder and slit stand are mounted on the same bed-plate, and a thick lead cover is laid over to prevent blackening through diffused rays. Calcite crystals alone have been used with this instrument. The measurement of the reflexion angle is carried out as follows. A fine slit (with gold edges) is adjusted, so that the normal from the rotating axis to the photographic plate passes through it. The crystal is placed on the table with its reflecting plane in the rotation axis. The crystal is then turned so that the normal slit-plate forms an angle with the crystal face approximately equal to the reflexion angle for the spectral line sought. This is done in two ways; in one case the plate-holder may be turned to the right side in order that the incoming pencil shall be reflected; in the other case a turning of the plate-holder to the left is necessary. This spectrograph is suitable for wave-lengths 0·5 Å.U. to 2·0 Å.U. The instrument has been tested on measurements of $\text{CuK}\alpha_1$. In a previous paper, using the vacuum spectrograph, the value $\lambda = 1537\cdot36\text{XU}$ was obtained; with the present instrument the value $\lambda = 1537\cdot44\text{XU}$ is found; the difference 0·005% is attributed to a lack of information of the temperature-coefficient of the lattice constant of calcite.

J. F. S.

The Radioactivity of the Water from the Principal Spring at Bagnoles-de-l'Orne and its Variations. P. LOISEL (*Compt. rend.*, 1919, **169**, 791—792).—The water of Bagnoles contains from 22×10^{-12} to 109×10^{-12} grams of dissolved radium per litre, the mean value being 68×10^{-12} grams per litre. The amount of radium emanation in solution varies from 0·0002—0·0015 microcurie per litre.

W. G

Application of the Thermionic Amplifier to Conductivity Measurements. R. E. HALL and L. H. ADAMS (*J. Amer. Chem. Soc.*, 1919, **41**, 1515—1525).—The use of an amplifier in conjunction with the telephone in the measurement of the resistance of solutions makes the determination of the point of balance on the bridge much simpler. Any ordinary telephone becomes a much more sensitive instrument with an amplifier than the best telephone without it. When a sensitive telephone is used, the current through the bridge may be reduced to a tenth of the value necessary without the amplifier, and the instrument will still have several times the sensitiveness it has without the amplifier. An electron tube may be used as a source of alternating current for conductivity measurements. Its advantages are its cheapness and the wide range of frequencies which may be obtained with it. A first harmonic is present in the current, which is noticeable at low frequencies, but which is not troublesome at a frequency of 1000 cycles or more. If, for any reason, it should be desired to use frequencies in conductivity measurements beyond the limit of the human ear, a telephone could still be employed to indicate the bridge balance by the use of the autodyne method. J. F. S.

Preparation of Conductivity Water. C. B. CLEVENGER (*J. Ind. Eng. Chem.*, 1919, **11**, 964—966).—The apparatus described is a modification of the Bourdillon still (T., 1913, **103**, 791); the steam, obtained from water containing phosphoric acid or potassium hydrogen sulphate, is led through a coil and trap, and then enters a vertical tin tube about 6 feet long, the inlet for the steam being at about the middle of the vertical tube. The latter is fitted with condensing jackets, one at the top and the other near the lower end, which is bent into the form of a trap and enters the containing vessel for the conductivity water. A current of pure air is admitted to the vertical tube through a side-tube just below the lower condensing jacket; this current of air ascends the vertical tube, mixes with the steam, and carries off any remaining impurities through the upper end of the tube. The various parts of the apparatus are made of tin-coated metal, and the upper end of the vertical tube is connected with absorption vessels for preventing the entrance of ammonia, etc. [See, further, *J. Soc. Chem. Ind.*, 1919, 928A.] W. P. S.

Behaviour of Electrolytic Ions in Solid Substances. Conductivity of Permutite Mixtures. A. GÜNTHER-SCHULZE (*Zeitsch. Elektrochem.*, 1919, **25**, 330—333).—The specific resistance and temperature-coefficient of twenty-one pure permutites have been determined by the method previously described (A., 1915, ii, 149). It is shown that in their preparation, in addition to an interchange of base, some permutites adsorb considerable amounts of salts. The specific conductivity of potassium-silver permutite and sodium-silver permutite of a series of compositions has been measured, and it is shown that in the former case the conductivity can be calculated according to the simple mixture

rule, whilst in the latter case this is only approximately true. On the assumption that the law of reciprocal influence of two salts with a common ion on the degree of ionisation holds, it follows that sodium, potassium, and silver permittite are dissociated to approximately the same extent.

J. F. S.

Is the Electrical Conductivity of the Elements Conditioned by the Presence of Isotopes? F. H. LORING (*Chem. News*, 1919, **119**, 199—200. Compare this vol., ii, 384).—A theoretical paper in which various points dealt with in the previous paper (*loc. cit.*) are discussed in the light of the publications of other investigators.

J. F. S.

Anodic Polarisation. II. A. SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 1349—1351).—An explanation of the phenomenon previously described (*ibid.*, 1918, **20**, 1121) is given. Iron can only exist in a state of internal equilibrium in a solution which contains no ferric ions. The presence of ferric ions disturbs the equilibrium, the more the greater the concentration of the ferric ions. The potential of iron is therefore less negative in a solution that contains ferric ions than in one which is free from ferric ions. In the solution with which the stated phenomenon was obtained, the iron consequently did not present the potential of internal equilibrium, but a less negative potential. In such a liquid, iron, when brought into solution, will change the concentration of the electrolyte in the neighbourhood of the electrode. The iron goes into solution exclusively as ferrous ion. During this anodic solution, the internal equilibrium is disturbed, as is indicated by the less negative potential, and, at the same time, the metal is surrounded by a liquid layer poorer in ferric iron than the rest of the solution. After the current has been broken, the iron approaches internal equilibrium with great rapidity, and on account of the decrease in ferric-ion concentration in its immediate neighbourhood, will exhibit a more negative potential than before polarisation. This state can, however, only persist for a short period, since the ferric ions diffuse from the outside into the boundary layer, and so the potential becomes less negative, and eventually reaches its initial value.

J. F. S.

Electrical Characteristics of Pigment Colloids. RUDOLF KELLER (*Kolloid Zeitsch.*, 1919, **25**, 60—62).—In works of reference on colloids, among others in that of Zsigmondy, it is stated that basic colour substances in colloidal solution travel towards the cathode, acid substances towards the anode, under the influence of an electric current. The author finds that this is not a general rule, for alkaline solutions of methylene-blue and acid magenta travel to the anode and acid solutions of the same substances travel to the cathode. The reason for this behaviour is probably that in the first place pigment colloids, which have neither strong acidic nor strong basic characteristics, obtain their electric charges, according to Cohen's rule, by virtue of the ratio of the dielectric

constant compared with that of water, and in the second place from the electric charges of the dispersion medium. J. F. S.

Table of P_H , H' and OH' Values corresponding with Electromotive Forces determined in Hydrogen Electrode Measurements, with a Bibliography. CARL L. A. SCHMIDT and D. R. HOAGLAND (*Univ. California Pub. Physiol.*, 1919, **2**, 23—69).—The table includes values of P_H from 0.034 to 14.032. The bibliography of 467 titles covers the entire field of hydrogen-ion concentration up to 1919. The methods for the determination of hydrogen-ion concentration are reviewed.

CHEMICAL ABSTRACTS.

Discharge Electrolysis. Electrical Colloid Syntheses. V. KOHLSCHÜTTER (*Zeitsch. Elektrochem.*, 1919, **25**, 309—323).—An electrical method for preparing colloidal metals is described which consists in electrolysing water with either direct or alternating current combined with a condenser circuit. The author terms the process "discharge electrolysis." Experiments are described in which colloidal copper is produced by the electrolysis of ordinary distilled water by means of direct current (96 volts) or alternating current (125/8000 volts), using two copper electrodes close together with a condenser in a parallel circuit. It is shown that when a discharge of at least 100 volts passes between two copper electrodes in distilled water, the cathode is disintegrated into fairly large particles, but if an oscillating parallel circuit is combined with the main circuit, the disintegration passes over, more or less completely, according to conditions, to the anode, and colloidal copper oxide is produced. Experiments with direct current show that an increasing capacity in the secondary circuit and a decreasing resistance in the main circuit increase the amount of disintegration, but, at the same time, the characteristic action of the oscillating circuit becomes more and more predominating. The disintegrated metal and the colloidal oxide are easily separated. The nature of the colloidal oxide depends on which of the two circuits predominates in its formation. The smaller the current strength and the capacity, the smaller are the colloidal oxide particles. The effect is produced because the electrolytic current covers the anode with a disperse oxide layer, and this is disintegrated by the spark discharge. When alternating current is used, the process is helped by a depolarising action of the cathodic component. J. F. S.

Auto-complexes in Solutions of Cupric Chloride and Cupric Bromide. STEWART BYRON WATKINS and HENRY GEORGE DENHAM (*T.*, 1919, **115**, 1269—1279).

Magneto-chemistry of Chromous and Oxychromic Salts. B. CARRERA and S. PIÑA DE RUBIES (*Anal. Fis. Quim.*, 1919, **17**, 149—167).—An account of a series of measurements of the magnetic susceptibility of solutions of chromous salts. The apparatus and the method of Quincke were employed. For the chromous

ion in sulphate and chloride solutions, the integral number 24 was obtained for the number of magnetons. The oxychromic salts of the formulæ $\text{Cr}_2\text{O}(\text{SO}_4)_2$ and Cr_2OCl_4 , each in the violet and the green modification, were also studied. Integral numbers of magnetons for these complex cations were not obtained.

W. S. M.

Maximum Temperature [Limit]. WALTHER JANKOWSKY (*Zeitsch. Elektrochem.*, 1919, 25, 325—328).—A theoretical paper in which, from a consideration of heat of reaction at medium temperatures, it is shown that this quantity is developed for the most part by a conversion of potential energy into heat. From this deduction, it follows that not only must an absolute zero of temperature exist, but that there must also be an absolute upper limit (maximum temperature). The absolute zero is defined as that temperature at which the energy content of a substance consists entirely of potential energy and at which a conversion of potential energy into heat is impossible. The maximum temperature is defined as that temperature at which the energy content consists entirely of heat and at which the conversion of heat into potential energy is impossible. All heat changes, inclusive of chemical reactions, must occur between these two temperature limits. In the neighbourhood of both points, the thermal properties of all substances approach the zero value. Both temperature limits are only reached asymptotically.

J. F. S.

Investigation of Mewes' Law of the Relation between the Volume of a Gas and the Temperature. RUDOLF MEWES and LUDWIG NEUMANN (*Zeitsch. Sauerstoff. Stickstoff. Ind.*, 1919, 11, 13—15; from *Chem. Zentr.*, 1919, iii, 149).—Some years ago, one of the authors proposed to replace Gay-Lussac's formula, $v_t = v_0(1 + \alpha t)$, by the expression $v_t - x = (v_0 - x)(1 + \alpha)^t$, or, approximately,

$$v_t = v_0(1 + \alpha)^t,$$

where $\log(1 + \alpha) = 0.00111$. At temperatures above 0° , and within not too narrow limits, the results agree closely with those of Gay-Lussac's formula, but the discrepancies increase with decreasing temperature; at -182° , for example, the ratio of the density to that at 0° is about 3 according to Gay-Lussac and about 2 according to Mewes. Investigations by others have tended to confirm the older formula; the authors have therefore re-examined the behaviour of air, nitrogen, oxygen, and hydrogen with diminishing temperature, and have been led to the conclusion that sources of error are to be found in the previous arrangements of all investigators, including their own. To eliminate such sources (partial liquefaction and surface condensation of the difficultly liquefiable gases), the ratio of the liquid portion to the total amount must be ascertained, which could be accomplished mathematically. It is found, however, that they do not give a satisfactory explanation of the divergencies between the experimental and calculated results; particularly in the case of hydrogen, they

can only exercise a slight influence on the value of the specific heat. H. W.

The Specific Heat of Air at Ordinary and Low Temperatures. KARL SCHEEL and WILHELM HEUSE (*Zeitsch. Sauerstoff Stickstoff. Ind.*, 1919, 11, 26—29; from *Chem. Zentr.*, 1919, iii, 148—149).—The previous determinations of the specific heat of air at low temperatures are confined to -77° , -102° , and -170° , and lead to the conclusion that the specific heat at atmospheric pressure is independent of the temperature. The authors' experiments have been performed with a specially constructed calorimeter, in which the loss of heat is reduced to very small dimensions. The apparatus and mode of experiment are fully described in the original. The authors find that the specific heat of air increases with decreasing temperature, and is approximately 5% greater at -183° than at the ordinary temperature. H. W.

Variation of the Specific Heat during Melting and the Heat of Fusion of some Metals. IITIRŌ IITAKA (*Sci. Rep. Tōhoku Imp. Univ.*, 1919, 8, 99—114).—The specific heats of the elements bismuth, lead, tin, zinc, sulphur, and sodium have been determined at several temperatures, both above and below the melting points. It is shown that the specific heat undergoes a discontinuous change during melting, which is generally positive, but in some cases the change is negative. The following values have been obtained: bismuth, c_s 0.0338, c_l 0.0356, Mc_s 7.02, Mc_l 7.40; lead, c_s 0.0358, c_l 0.0340, Mc_s 7.43, Mc_l 7.04; tin, c_s 0.0662, c_l 0.0615, Mc_s 7.88, Mc_l 7.31; zinc, c_s 0.110, c_l 0.121, Mc_s 7.20, Mc_l 7.91; sulphur, c_s 0.200, c_l 0.199, Mc_s 6.41, Mc_l 6.39; sodium, c_s 0.330, c_l 0.347, Mc_s 7.59, Mc_l 7.98. The specific heat of the solid at the melting point is designated by c_s , that of the liquid at the same temperature by c_l , and the atomic heats by Mc_s and Mc_l respectively. The atomic heat is almost constant and independent of temperature for the liquid elements. The atomic heat at constant volume has been calculated for the temperatures 0° , 100° , 200° , 300° , and the melting point. The values at the melting point are: bismuth 6.90, lead 6.58, mercury 5.90, tin 7.40, and zinc 6.22. The latent heat of fusion has also been calculated from the experimental results, and the following values obtained: bismuth 12.24, lead 5.53, tin 13.38, zinc 23.1, sulphur 13.2, and sodium 26.0. J. F. S.

Calculation of the Latent Heat of Vaporisation from Critical Data. W. HERZ (*Zeitsch. Elektrochem.*, 1919, 25, 323—324).—By means of the equations $L = p_k \cdot T_s / T_k \cdot d_k$ and $L = 2/3 \cdot p_k / d_k$, the author shows that the latent heat of vaporisation of non-associated liquids may be calculated. The symbols have the following significance: L is the latent heat of vaporisation, T_s is the boiling point in degrees absolute, T_k and p_k the critical temperature and critical pressure respectively, and d_k is the critical density. The calculations have been made for twenty-

two organic liquids and three inorganic liquids, and it is shown that there is a moderate agreement between the calculated and experimental results. In the case of water and methyl alcohol, which are associated, there is a wide divergence between the calculated and experimental values, but in that of acetic acid, which is also associated, the two agree to within 10%. J. F. S.

A Vapour Pressure Equation. GEORGE W. TODD and S. P. OWEN (*Phil. Mag.*, 1919, [vi], **38**, 655—660).—A mathematical paper in which the equilibrium of a vapour in contact with its liquid is considered on the assumptions that all vapour molecules striking the liquid surface penetrate it, and only those liquid molecules which have a velocity greater than a definite critical value, whatever their angles of impact with the surface, penetrate it and leave the liquid. Vapour-pressure equations $p = A\rho e^{-B/\theta} (1 + B/\theta)$ and $p = A'e^{-B/\theta} (1 + B/\theta)$ are deduced, in which p is the vapour pressure and ρ the density at a temperature θ , B is the collision frequency of a molecule of velocity c . The former equation is useful where the density values are known up to the critical temperature, and the latter for those cases where the density is only known over moderate ranges of temperature. The equations are tested in the case of water, mercury, benzene, bromine, and ethyl ether, where a fairly good agreement with experiment is found. The average kinetic energy of a molecule at the critical temperature (θ_c) is given by the expression $\frac{1}{2}mc_1^2 = \theta_c/273(5.5 \times 10^{-14})$ erg. A table of values of $\log A'$ and B obtained from vapour-pressure measurements is given for thirteen liquids, and it is shown that the value of B obtained from the critical temperature is one-third to one-fourth of the value obtained from the equation. J. F. S.

Simple Method of Determining the Velocity of Sound in Gases and Vapours and the Density of Gases. P. BRÄUER (*Zeitsch. physikal. Chem. Unterr.*, 1919, **32**, 1—6; from *Chem. Zentr.*, 1919, iii, 114—115).—The experiment is performed in thin-walled tubes, 2—3 cm. in diameter and at most 60 cm. long, which are filled with the gas or vapour. The note emitted when the tube is struck is matched by that of a monochord string, and the experiment is repeated with the tube full of air. The frequencies of the notes are inversely proportional to the lengths of the strings. The velocity of sound and the density of the gas are readily calculated. The procedure is as accurate as that proposed by Victor Meyer, and can be more rapidly carried out. H. W.

Absolute Determination of the Coefficients of Viscosity of Hydrogen, Nitrogen, and Oxygen. KIA-LOK YEN (*Phil. Mag.*, 1919, [vi], **38**, 582—596).—The absolute viscosities of hydrogen, nitrogen, and oxygen have been determined at 23.00° and 760 mm. pressure by Millikan's constant deflexion apparatus, previously described (Gilchrist, *Phys. Rev.*, 1913, **1**, 124; Harrington, *ibid.*, 1916, **8**, 738). The results obtained are: hydrogen, $\eta \times 10^7 =$

882.16 (20 expts.); oxygen, $\eta \times 10^7 = 2042.35$ (20 expts.); and nitrogen, $\eta \times 10^7 = 1764.80$ (21 expts.). An accuracy of 0.15% is claimed for the results. J. F. S.

Adsorption of Gases at Low and Moderate Concentrations. I. Deduction of the Theoretical Adsorption Isostere and Isotherm. II. Experimental Verification of the Form of the Theoretical Isosteres and Isotherms. A. M. WILLIAMS (*Proc. Roy. Soc.*, 1919, [A], **96**, 287—297).—The theoretical form of the adsorption isostere is deduced and found to be $\log a/c = B + A/T$, where A and B are functions of a alone. The theoretical form of the adsorption isotherm is found to be $\log a/c = A_0 - A_1 a$, where A_0 and A_1 are functions of the temperature only. These equations are tested by means of the data of various observers on the gases, argon, methane, carbon dioxide, ammonia, nitrogen, and carbon monoxide. A satisfactory agreement is found in the case of the former equation for gases above or near the critical temperature. In the latter case satisfactory agreement is found up to moderate adsorptions of gases above their critical temperature. J. F. S.

Adsorption of Gases at Low and Moderate Concentrations. III. Experimental Verification of the Constants in the Theoretical Adsorption Isostere. A. M. WILLIAMS (*Proc. Roy. Soc.*, 1919, [A], **96**, 298—311. Compare preceding abstract).—The constants of the equation for the theoretical adsorption isostere are deduced from the observations of many observers for the gases argon, ethylene, carbon dioxide, methane, carbon monoxide, and nitrogen. The form of theoretical adsorption isostere has been determined at zero concentration for the above-named gases above the critical point. The relationship among the constants is in good agreement with the theory based on the existence of a thin surface layer. The range of molecular attraction is determined and found to vary from 3.2 to 4.1×10^{-8} cm. J. F. S.

Theory of Adsorption of Electrolytes. The Adsorption of Organic Dyes. LEONOR MICHAELIS and PETER RONA (*Biochem. Zeitsch.*, 1919, **97**, 57—84).—The salts of basic and acid dyes have been employed in the study of adsorption by various substances. In the case of charcoal the cations and anions are adsorbed in equivalent proportions. Slight deviations from this principle can be explained by the impurity of the charcoal. When insoluble salts are used as adsorbents there is an exchange of anions or cations between the adsorbents and the substance adsorbed. Insoluble acid or basic oxides have shown no perceptible adsorbing capacity. In no case was a "hydrolytic" adsorption of the salts observed, that is, where the salts were split into acid and base, and the adsorption of one ion only took place. The nature of the adsorption capacity of carbon is discussed. S. S. Z.

Adsorption of H- and OH-Ions and the Ions of the Heavy Metals by Charcoal. PETER RONA and LEONOR MICHAELIS (*Biochem. Zeitsch.*, 1919, **97**, 85—97).—The H- and OH-ions are

adsorbed by charcoal to the same extent. The amount of mercuric chloride adsorbed by charcoal may, in the presence of chlorides, be diminished by as much as 60%. S. S. Z.

Electrification of Water and Osmotic Pressure. JACQUES LOEB (*J. Gen. Physiol.*, 1919, **2**, 87—106).—It is shown for the amphoteric electrolytes, aluminium hydroxide, and gelatin, that in the presence of an acid salt water diffuses through a collodion membrane into a solution of these substances as if its particles were negatively charged, whilst water diffuses into solutions of these electrolytes, when they exist as salts of univalent or bivalent metals, as if the particles of water were positively charged. The turning point for the sign of the electrification of water seems to be near or to coincide with the isoelectric point of these two ampholytes, which is about $2 \times 10^{-5} N$ for gelatin and $10^{-7} N$ for aluminium hydroxide.

Apparently positively charged water diffuses with less rapidity through a collodion membrane into a solution of calcium or barium gelatinate than into a solution of lithium, potassium, sodium, or ammonium gelatinate of the same concentration of gelatin and hydrogen ions, and negatively charged water diffuses with less rapidity through a collodion membrane into a solution of gelatin sulphate than into a solution of gelatin chloride or nitrate of the same concentration of gelatin and hydrogen ions.

If osmotic pressure is defined as the additional pressure on the solution required to cause as many molecules of water to diffuse from solution to the pure water as diffuse simultaneously in the opposite direction through the membrane, it follows that the osmotic pressure cannot depend only on the concentration of the solute, but must also depend on the electrostatic effects of the ions present, and that the influence of the ions on the osmotic pressure must be the same as that on the initial velocity of diffusion. This assumption was tested in experiments with gelatin salts, for which a collodion membrane is strictly semipermeable, and the tests confirmed the expectation. J. C. D.

Hydrogen and Hydroxyl Ion Equilibria in Solutions. II. W. LÖFFLER and K. SPIRO (*Helv. Chim. Acta*, 1919, **2**, 533—550. Compare Asher and Spiro, *Ergb. Physiol.*, 1909, **8**, 254).—From experiments, carried out by the indicator method, on the changes in the hydroxyl and hydrogen-ion concentration in solutions of glycine brought about by neutral substances of physiological importance, such as glycerol, dextrose, and ethylene glycol, it is shown that these substances are capable of forming complex salts. This is seen particularly in the case of glycine. Such solutions, which are non-sensitive to a change in their alkalinity, change their concentration of hydrogen and hydroxyl ions by shaking with animal charcoal in the sense that they approach neutrality. The adsorption by charcoal is to be regarded as a process of solution, and it is shown that a different decomposition of acid salts in aqueous solution is brought about by shaking with animal charcoal. J. F. S.

[Behaviour of Non-aqueous Solutions of Salts.] R. BEUTNER (*Zeitsch. Elektrochem.*, 1919, **25**, 328—329, 329—330. A. THIEL, *ibid.*, 329).—Polemical. Beutner answers Thiel's criticism (this vol., ii, 388) of his paper (this vol., ii, 263). In a second paper Thiel further criticises Beutner's conclusions, and in a third paper Beutner gives a final reply to Thiel. J. F. S.

Crystallisation Phenomena in Formaldehyde-Gelatin Jellies. W. MOELLER (*Kolloid. Zeitsch.*, 1919, **25**, 67—74).—The crystallisation of formaldehyde gelatin jellies has been experimentally studied. It is shown that the crystallisation phenomena (formation of sphäro-crystals) are to be attributed to the orienting influence of the formaldehyde condensation and polymerisation products on the α -gelatin micellæ. In the observed spherical crystal formation the individual micellæ are arranged radially in the form of concentric spherical sheaths, and behave optically as a crystalline drop. The numerous forms which differ from the above are attributed to a deformation brought about by the tensions set up while the jelly is drying, whereby the arrangement of the micellæ approaches more and more to a fibrous structure. Sphäro-crystals produced by varying the experimental conditions often exhibit this fibrous structure. J. F. S.

Coagulation. I. The Velocity of Gelation and Hydrolysis of Gelatin Sol. RINOSUKE SHÖJI (*Biochem. J.*, 1919, **13**, 227—238).—The equation $\eta - \eta_i = \mu t / 1 + (\mu / \lambda) t$ is given, which represents the change in viscosity of gelatin sol with respect to time in the early stages of gelation, and the bearing of this equation on the nature of gelation is discussed at some length.

Another equation, $2k\tau = 1/(\eta_i - \eta_{i\infty})^2 - 1/(\eta_0 - \eta_{i\infty})^2$, is given which represents the change in viscosity of gelatin sol with respect to time in the course of its hydrolysis caused by heating.

J. C. D.

Coagulation Process [of Colloids]. H. R. KRUYT and JAC. VAN DER SPEK (*Kolloid Zeitsch.*, 1919, **25**, 1—20).—The coagulation of arsenic sulphide and ferric hydroxide sols has been investigated. It is shown that the relationship between coagulation value and the colloidal concentration for arsenic sulphide sols varies as follows: the coagulation value for a univalent precipitating ion increases with increasing dilution, for a tervalent ion it decreases, and for a bivalent ion there is a slight decrease. The reduction of the degree of dispersion by boiling or by a change in the original concentration leads to an augmentation of the coagulation value for potassium and barium ions, but to a reduction for aluminium ions. These phenomena may be explained by the hypothesis that the colloidal particles may combine as they approach one another through their Brownian movements. The reduction of the total surface conditions a reduction of the quantity of electrolyte necessary to reach a definite adsorbed quantity. Dilution and a reduction in the dispersity cause a separation of the particles and

reduce the chances of their collision, and under these conditions a smaller charge is necessary for their coagulation. Similar experiments were made with ferric hydroxide sol, but here both sodium hydroxide and disodium phosphate behave irregularly. J. F. S.

Colloidal Processes in the Setting of Plaster. Structure of Plaster of Paris. I. TRAUBE (*Kolloid. Zeitsch.*, 1919, 25, 62—66).—The velocity of the setting of the hemihydrate of calcium sulphate has been investigated, and the influence of the addition of salts, acids, bases, and neutral substances to the soft plaster on the rate of setting has been observed. Ten grams of calcium sulphate were rapidly mixed with stated quantities of water or solutions of other substances, the mixture poured on to a glass plate, and the time noted when it had completely set. With 4 c.c. of 0.5*N*-potassium chloride, setting occurred almost instantaneously, with 5 c.c. in 2.5 minutes, with 7 c.c. in 4 minutes, with 15 c.c. the mixture had not set in 40 minutes. Using 7 c.c. of saturated potassium chloride solution, setting occurred in 12 minutes; 7 c.c. of *N*/2-solution required 4.5 minutes, 7 c.c. of 0.25*N* required 5.5 minutes, and 7 c.c. of *N*/16 19 minutes. There is, therefore, a maximum setting velocity for medium concentrations. In experiments with other salts, it is shown that the influence of the anion is very small, but that of the cation is all-important. The order in which the cations influence the setting is the reverse of the order in which they precipitate colloids from solutions; thus the univalent cations accelerate the setting most. From these experiments, it is concluded that the combination of the hemihydrate of calcium sulphate with water is brought about in the first place by gel formation. A similar series of experiments was made with 7 c.c. of various acids in *N*/2-concentration. The order of setting from the most rapid is hydrochloric acid, oxalic acid > sulphuric acid > trichloroacetic acid > tartaric acid > boric acid > phosphoric acid > dichloroacetic acid > chloroacetic acid > acetic acid > propionic acid > citric acid. The addition of 7 c.c. of *N*/2-potassium hydroxide effected setting in about the same time as hydrochloric acid. Non-conductors, such as chloral hydrate, amyl alcohol, propionitrile, mannitol, paracetaldehyde, methyl alcohol, and methyl ethyl ketone had no influence on the rate of setting. Gelatin and gums retarded the rate of setting. By allowing ferric chloride to diffuse through the set plaster towards potassium ferrocyanide which is diffusing in the opposite direction, structures of the same nature as the protoplasm structure are obtained. Agate structures and others of both geological and physiological interest have also been obtained. The author's experiments confirm in every detail the views on the nature of the setting of cements put forward by Cavazzi (A., 1913, ii, 136). J. F. S.

Molecular Mechanism of Colloidal Behaviour. II. The Swelling of Fibrin in Alkalis. RICHARD C. TOLMAN and RUSSEL S. BRACEWELL (*J. Amer. Chem. Soc.*, 1919, 41, 1503—1510. Compare Tolman and Stearn, this vol., ii, 101).—The swelling of

fibrin in solutions of sodium hydroxide, potassium hydroxide, and ammonia of various concentrations, and also of similar solutions containing potassium chloride, potassium sulphate, and sucrose has been investigated. It is shown that the swelling in solutions of sodium and potassium hydroxides reaches a maximum at very low concentrations—less than $N/20$; in the same way, the adsorption of alkali reaches a maximum at low concentrations, and a further increase in the concentration of the alkali brings about no change in the adsorption, but a reduction in the amount of swelling. In the case of ammonia solutions, it is shown that both the amount of swelling and the adsorption increase with increasing concentration up to $0.8N$ without reaching a maximum. The addition of neutral salts reduces the swelling in the same way as increase in the concentration of the alkali itself after the maximum has been reached, and also increases the adsorption. Sucrose has no effect on the swelling of fibrin, but water is adsorbed from the solution by the fibrin.

J. F. S.

Molecular Mechanism of Colloidal Behaviour. III. Chemical Nature of the Adsorption of Acids and Alkalis by the Protein Molecule. RUSSEL S. BRACEWELL (*J. Amer. Chem. Soc.*, 1919, **41**, 1511—1515. Compare preceding abstract).—A theoretical paper in which it is shown that the acid-adsorbing power of proteins is mainly due to the free amino-groups present, that is, adsorption consists in the formation of weak compounds between the amino-group and the acid. Attempts to formulate a similar hypothesis for alkali adsorption were unsuccessful.

J. F. S.

Colour of Colloids. VIII. WILDER D. BANCROFT (*J. Physical Chem.*, 1919, **23**, 445—468. Compare this vol., ii, 324).—A continuation of the previously published discussion. In the present paper, absorption colours, colours of turbid media, prismatic dispersion colours, grating colours, and colours of thin films are discussed in their relationships with the colour of birds and butterflies.

J. F. S.

Colloidal Electrolytes: Soap Solutions as a Type. JAMES WILLIAM MCBAIN, (MISS) MARY EVELYN LAING, and ALAN FRANCIS TITLEY (*T.*, 1919, **115**, 1279—1300).

The Degree of Hydration of the Particles which Form the Structural Basis of Soap Curd, Determined in Experiments on Sorption and Salting Out. JAMES WILLIAM MCBAIN and (MISS) MILLICENT TAYLOR (*T.*, 1919, **115**, 1300—1308).

Simultaneous or Successive Chemical Decompositions Provoked by Physical Agents. J. A. MULLER (*Compt. rend.*, 1919, **169**, 793—794).—In simultaneous decompositions of the first order, the ratios of the two coefficients of decomposition, at the end of any given time, are equal to the ratios of the corre-

sponding velocity constants. The subject is discussed mathematically, and the equations given, together with the results of chemical analyses, provide a means of determining the nature and order of the changes produced in pyrogenic decompositions. W. G.

The Interaction of Chlorine and Hydrogen. The Influence of Mass. DAVID LEONARD CHAPMAN and JOHN REGINALD HARVEY WHISTON (T., 1919, 115, 1264—1269).

Comparison of the Temperatures of Explosion calculated from Specific Heats with the Temperatures of Explosion calculated from Explosive Pressures. HENRI MURAOUR (*Compt. rend.*, 1919, 169, 723—726).—As the result of experiments with mixtures of tolite and ammonium nitrate, it is shown that the explosion temperatures, as calculated from the specific heats of Mallard and Le Chatelier or of Sarrau, are markedly higher than the figures obtained by calculation from the manometric tables, except where the temperatures are above 3000°. The results obtained by either method in the region 1500—1700° are certainly below the actual temperatures. The results, as calculated from the manometric pressure in this region, are so low as to indicate either that the value of the pressure must be modified or that the law used for expressing the compressibility of gases at high temperatures and pressures is incorrect. Over the temperature range 1300—2700° the temperatures, calculated from Schreiber's specific heats, are in accord with the temperatures calculated from the pressure tables of the French research laboratories. W. G.

Ignition of Gases by Hot Wires. W. M. THORNTON (*Phil. Mag.*, 1919, [vi], 38, 613—633).—The ignition of the gases hydrogen, methane, ethane, pentane, ethylene, carbon monoxide, coal gas, and vapours of methyl alcohol, ethyl alcohol, diethyl ether, and benzene in air by electrically heated wires of platinum, nickel, iron, tungsten, molybdenum, gold, and silver of various diameters and at various temperatures has been experimentally investigated. It is shown that ignition by hot wires occurs when the generation of heat per unit length has reached a certain definite value. At low temperatures, this is removed by convection, when a steady state is reached, and is almost independent of the diameter of the wire. Ignition is independent of gas pressure, of the heat of combustion of the mixture, of the proportion of gas present, and for any given metal, independent of the nature of the combustible molecule so far as it is affected by change of diameter, hydrogen and platinum being exceptions. That is, since previous heating of the gas does not affect ignition temperatures, it is, on the whole, independent of every external physical or chemical variable. The source of ignition must therefore be sought in some phenomenon depending strictly on the rate of generation of heat by the passage of the current, but occurring, if not within the surface layer of the metal itself, so near to it that the ordinary gas laws are not

operative. Oxygen is the only active component of all the mixtures, and it can be inferred that the mechanism of hot wire ignition is an attack on oxygen either within the wire or by positive ions of combustible gas just ejected from it, for the temperatures at which surface action begins are lower than those which start combination of gases separately heated to a point at which they explode on mixing. Electric and magnetic fields have no influence on surface combustion observable by the phenomena of ignition. Compared with spark ignition, hot wire ignition is singularly constant in type.

J. F. S.

The Determination of Ignition-temperatures by the Soap-bubble Method. ALBERT GREVILLE WHITE and TUDOR WILLIAMS PRICE (T., 1919, 115, 1248—1264).

Indirect Analysis of Gas Hydrates by a Thermodynamic Method and its Application to the Hydrate of Hydrogen Sulphide. I. and II. F. E. C. SCHEFFER and G. MEYER (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, 21, 1204—1212, 1338—1348). —In earlier papers (Scheffer, A., 1911, ii, 264, 870) it is shown that in solutions of hydrogen sulphide a four-phase equilibrium exists between a hydrate, two liquid phases (water and hydrogen sulphide), and gas. The analysis of the hydrate leads to a water content between 5.1 and 5.4 molecules per molecule of hydrogen sulphide. It is likely that the accepted value $5\text{H}_2\text{O}$ is not correct, and, with the object of determining the true composition, the authors have developed, on thermodynamical considerations, a method of indirectly ascertaining the composition of such hydrates. The method is briefly as follows. A binary system is taken of which one component, A , is gaseous over a definite temperature range, and the second, B , is near its melting point, and is not markedly volatile. On increase of pressure, a solid compound can form from the gas A and the solid B . In the melted component B , the gas is soluble neither as such nor as compound. In the equilibria set up, the component A appears as a gas (G) and bound in the compound S ; the component B occurs free as solid, S_B , and liquid, L , and bound in the compound S . The three-phase lines $S_B LG$ and $SS_B L$ coincide with the melting-point line of B . The transformation is indicated by the change $S_B \rightleftharpoons L$ on both three-phase lines, and is the same as on the melting-point line of pure B . The triple point of B lies near the T axis; the sublimation and boiling-point line of B practically coincides with the T axis. If the compound is indicated by AB_n , the transformations on the two other three-phase lines are indicated by $AB_n \rightleftharpoons A + nB - E_1$ (on $SS_B G$) and $AB_n \rightleftharpoons A + nB - E_2$ (on SLG). The difference of the two energies E_1 and E_2 is equal to the heat of fusion of n molecules of B . $E_2 - E_1 = nQ$ when the heat of fusion of B is Q per molecule. Making use of the Clapeyron equation, the value of $E_2 - E_1$ can be determined if the three-phase lines $SS_B G$ and SLG are known. This method is applied to the system hydrogen sulphide-water, and the lines $SS_B G$ and SLG are experimentally determined, and from

the data thus obtained the value of n is found to be 6. Hence the crystalline hydrate of hydrogen sulphide is $\text{H}_2\text{S}\cdot 6\text{H}_2\text{O}$.

J. F. S.

Theory of the Velocity of Reaction in Gases. KARL F. HERZSFELD (*Ann. Physik*, 1919, [iv], 59, 635—667; *Zeitsch. Elektrochem.*, 1919, 25, 301—304).—A theoretical paper in which the velocity of reactions of the first and second order is discussed mathematically. In an historical introduction, the work of Trautz (A., 1909, ii, 557, 651), among others, is discussed. It is shown that, in developing a systematic conception of gas reactions, the introduction of a retardation is helpful. That is, a condition based on the consideration of whether an atom can react directly or whether it must first break away from an existing combination before reaction is possible. In exothermic reactions with one or no retardation, every collision of the molecules is operative, independently of the temperature, whilst with two retardations only a small fraction of the collisions is operative, and these are dependent on the temperature. In the case of endothermic reactions, only one example of a retardation is known, namely, the formation of hydrogen bromide; here it is shown that, for a collision to be operative, the kinetic energy, which depends on the opposing velocities of the colliding particles, must be greater than the heat of the reaction. The influence of the internal energy makes itself obvious, inasmuch as only a definite proportion of the reacting substances can be converted into the products of the reaction. Therefore in exothermic reactions the number of operative collisions is to be multiplied by a factor which depends on the internal specific heat. The reaction formulæ deduced are applied to the work of Bodenstein (A., 1899, ii, 637) and Lind (A., 1907, ii, 76) on the formation of hydrogen bromide, and very good agreement is shown to exist.

J. F. S.

The Velocities of Combination of Sodium Derivatives of Phenols with Olefine Oxides. II. DAVID RUNCIMAN BOYD and (MISS) DORIS FELTHAM THOMAS (T., 1919, 115, 1239—1243).

The Rate of Hydrolysis of Methyl Acetate by Hydrochloric Acid in Water-Acetone Mixtures. GEORGE JOSEPH BURROWS (T., 1919, 115, 1230—1239).

Kinetics of Reactions with Substituted Malonic Acids. A. L. BERNOULLI and W. WEGE (*Helv. Chim. Acta*, 1919, 2, 511—532).—The kinetics of the scission of carbon dioxide by heat from malonic acid or methyl-, ethyl-, allyl-, benzyl-, phenyl-, diallyl-, dimethyl-, methylethyl-, diethyl- and dipropyl-malonic acids have been studied at 100° . The formation of acetic acid from an aqueous solution of malonic acid, over the temperature range 75 — 110° , is a strictly unimolecular reaction. By means of graphic extrapolation, it is shown that the lower limit of measurable change

lies at 66° . With the single exception of dipropylmalonic acid, in which case the value of k is not satisfactory, it is shown that all the substituted malonic acids are decomposed at 100° in aqueous solution, according to a unimolecular equation. Substituents, in the malonic acids, with either one or more double bonds, increase the velocity of decomposition, whilst substituents without double bonds reduce the rate of decomposition. The accelerating action of the double bond increases with the number and also with the nearness to the methylene group of the malonic acid; thus, the phenyl group accelerates the velocity more than the benzyl group. The entrance of a second substituent, similar or dissimilar, strongly decreases the rate of decomposition; thus, diallylmalonic acid decomposes with about half the velocity of allylmalonic acid. A parallelism is shown between the thermal stability of these substances (measured by the heat of formation) and the kinetic stability (measured by the reciprocal of the reaction velocity).

J. F. S.

The Rhythmic Evolution of Carbon Monoxide and the Constant of Accumulation. TOKIHARU OKAYA (*Proc. Phys. Math. Soc. Japan*, 1919, [3], 1, 43—51).—The author has previously suggested that in the case of the rhythmic precipitation of silver chromate in gelatin, there must exist certain relations between the concentrations of the reacting ions to determine the physical state at the moment of precipitation, and concluded that to precipitate silver chromate it is only necessary that the amount of "accumulation product" of the ions should attain a definite value, H^1 , which is constant throughout. In the present paper, the phenomenon of the rhythmic evolution of carbon monoxide produced by the dehydration of formic acid by sulphuric acid is satisfactorily explained by the notion of the "accumulation product." It is also shown that the reaction is one of the first order. The author points out that the existence of the quanta in natural phenomena is not limited to energy only. The present case and Liesegang's phenomena are but examples of such types of natural phenomena.

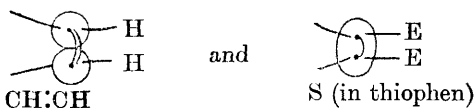
CHEMICAL ABSTRACTS.

Size and Shape of the Electron. ARTHUR H. COMPTON (*Physical Rev.*, 1919, 14, 20—40).—Assuming as proved that the amount of radiation of short wave-length scattered by various elements is proportional to the atomic number of the element, and accepting Thomson's assumption that the electron is a point charge, the scattered energy should be as great as that calculated from the Thomson equation. Actually, it is considerably less, sometimes as low as one quarter of the theoretical value. Unless a pulsation theory for these rays is abandoned, the discrepancy can only be explained on the assumption that the electron is comparable in magnitude with the wave-length of the shortest rays, or 2×10^{-10} cm. Three types of electrons are suggested, and the scattering is calculated for each type. All three satisfactorily fulfil the requirements. Type I, rigid spherical shell; type II,

flexible spherical shell; type III, flexible spherical ring. On still another count, a point charge electron is inadequate to account for the fact that emergent scattered radiation is more intense than incident radiation. It is necessary to assume an independent rotational activity of the electron, which type III above seems best suited to admit.

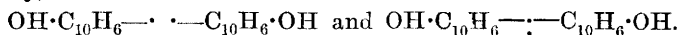
CHEMICAL ABSTRACTS.

Valency Centres. O. HINSBERG (*J. pr. Chem.*, 1919, [ii], 99, 232—238).—An extension of ideas previously advanced (A., 1916, i, 725; 1917, ii, 173, 461; 1918, ii, 106).—The theory deals with the elements of the first, second, fourth, sixth, and eighth groups of the periodic system, and it is assumed that one valency centre is present in the first four elements of each series and two valency centres in the four succeeding elements. The discontinuity of the physical properties of the elements in a series is conditioned by the occurrence of the second valency centre from the fifth group onwards, which causes a marked depression in melting and boiling points. In the formation of compounds with negative elements, the total valency of the elements of the fifth to seventh groups is utilised, whilst with positive elements or groups only the differential valency is used; the occurrence of elements of no valency appears to be merely an extension of the process of equalisation of the valencies of the two centres, the commencement of which is already apparent in the fifth to seventh groups. The ability to form ions, which is proper to many elements of the sixth and seventh groups, is probably due to the tendency of the atoms to form a particularly stable system by internal equalisation, in which four electrons are attached to each nucleus, or eight electrons are contained in a ring. The capability of forming onium compounds, as exhibited by nitrogen, sulphur, iodine, etc., depends on the presence of two valency centres, and therefore occurs solely in the right half of the periodic system. The equivalence of the sulphur atom to the $\text{CH}:\text{CH}-$ group in the formation of ring compounds (for example, thiophen and benzene) is explained by the formulæ:



in which the two hydrogen atoms of the group $\text{CH}:\text{CH}$ are replaced in the sulphur atom by two valency electrons (E), which are not compensated within the atom.

A number of cases among sulphur compounds are known, in which the isomerism can only be explained with difficulty if the presence of a single valency centre in the sulphur atom is assumed; if, however, two valency centres are present, the difficulty is removed. Thus the isomeric β -naphthol sulphides, m. p.'s 216° and 152° respectively, can be formulated:



The molecular complexity of the metalloids can be explained by

assuming that the partial equalisation of the two valency systems which occurs within the atoms can also take place between different atoms.

H. W.

Isomorphism, Isosterism, and Co-valence. IRVING LANGMUIR (*J. Amer. Chem. Soc.*, 1919, **41**, 1543—1559).—The octet theory of valency indicates that if compounds having the same number of atoms have also the same total number of electrons, the electrons may arrange themselves in the same manner. In this case the compounds or groups of atoms are said to be isosteric. Such compounds should show remarkable similarity in their physical properties, that is, in those properties which do not involve a separation of the atoms in the molecule. Thus O^{--} , F^- , Ne , Na^+ , and Mg^{++} are isosteric, as also are $N_2 \cdot CO \cdot CN^-$ and CH_4 and NH_4^+ . In cases where isosteric groups have the same electric charges the properties are directly comparable; thus, N_2 and CO , N_2O and CO_2 , KN_3 and $HCNO$ are nearly alike in all their physical properties. When the charges are dissimilar the similarity may manifest itself between properly chosen compounds, thus, KNO_3 and $CaCO_3$. The following cases of crystalline isomorphism are predicted by the octet theory and found to be in accordance with experimental observation: NaF and MgO , KN_3 and $KNCO$, KNO_3 and $SrCO_3$, $KClO_4$ and $SrSO_4$, $NaHSO_4$ and $CaHPO_4$, $MnSeO_4 \cdot 2H_2O$ and $FeAsO_4 \cdot 2H_2O$. Many other pairs are predicted, but have not yet been experimentally investigated. The theory of isosterism makes the deduction of certain relationships a very simple matter. Thus since argon is an isostere of the potassium ion, and methane is an isostere of the ammonium ion, it follows that the potassium and ammonium ions must have similar properties because argon and methane are nearly alike in physical properties. Similarly, the relationship between argon and nitrogen enables the tracing of an equally close relationship between cyanogen and chlorine ions. The experimental data prove that the crystalline form of substances depends on the structure as given by the octet theory, thus indicating that this theory gives a true picture of the constitutions of crystalline solids. The following conclusions are drawn: (1) the co-valency of sodium, potassium and chlorine (in chlorides) is zero. (2) The co-valency of the central atom is 4 in nitrates, carbonates, sulphates, perchlorates, phosphates, permanganates, chromates, selenates, and borofluorides. (3) Carbonates and sulphites are not isomorphous, the co-valency of the central atom being 4 and 3 respectively. (4) Nitrates and chlorates are not isomorphous, the co-valency of the chlorine being 3 in chlorates.

J. F. S.

New Hypotheses as to Different States of Matter. N. T. BACON (*J. Physical Chem.*, 1919, **23**, 469—477).—A theoretical paper in which it is shown that in the solid and liquid conditions matter is virtually incompressible, although under very high pressure, but constantly increasing in volume with increasing temperature, and for the liquid state with this condition continuing up to the critical point, except that near the critical point the apparent

compressibility of the liquid phase may be increased by solution of vapour molecules. The molecule, therefore, is constantly increasing the diameter of its sphere of influence as temperature increases up to the critical point. At this point the spheres of influence of the molecule of liquid and of vapour have the same size, since both forms of matter occupy the same space and have the same density. At the critical point the volatile form is at the dividing line between a saturated vapour and a true gas, and the vapour cannot act as a true gas because the spheres of influence of its molecules are in three dimensional contact, thus precluding translatory motion. Although the molecules in the liquid state continue to increase the dimensions of their spheres of influence with advancing temperature in spite of increasing pressure, nevertheless gaseous molecules can be materially compressed so as to occupy a smaller volume than at the critical point even at temperatures well above the critical temperature. Hence the spheres of influence of a true gas decrease with increasing temperature so as to allow a free path and thus cause them to follow Boyle's Law. The effect of the dissolved barium sulphate in a saturated aqueous solution is considered. Here a single molecule of barium sulphate (that is, one barium ion and one sulphate ion) so influences 10,000,000 water molecules that they are incapable of dissolving more barium sulphate, and imparts to the water a much higher conductivity; all this when the barium sulphate in solution can only come into contact with a small fraction of the water molecules. The author considers that the solution of barium sulphate up to its saturation point brings about a virtual expansion of the water molecules so as practically to fill up all the intermolecular spaces in the solvent and consequently leave no further room for additional barium sulphate. The conductivity of the barium sulphate solution he attributes to the barium sulphate breaking up into an enormous number of electrons, each having the characteristic periodicity of barium sulphate, and these so permeate the solvent that each molecule of this is in some way in contact, periodically at least, with such particles, so as to maintain an equilibrium relation. In the case of hydrolysis the complicated periodicity of the salt becomes too extended, so that part of the solute loses coherence and the fractions revert to their simpler, although related, periodicity, each in its own condition as if the other were not present. J F. S.

Automatic Mercury Pump, with Device for Collecting the Aspirated Gases. A. BEUTELL and P. OBERHOFFER (*Chem. Zeit.*, 1919, **43**, 705—706).—In the mercury pump previously described (A., 1911, ii, 105) the authors have introduced a vessel at the base of the tubes for collecting the gases drawn off, which are then passed into a measuring burette and an Orsat gas-analysis apparatus. The speed of the pump has been increased by allowing the mercury to drop through two tubes, and the device for preventing fracture of the tubes by the falling mercury has been modified.

W. J. W.

Inorganic Chemistry.

Reaction between Hydrogen and Bromine. J. A. CHRISTIANSEN (reprint from *D. K. Danske Videnskabernes Selskat. Math. fys. Medd.*, 1919, 1, 14).—A theoretical paper in which it is shown from the experiments of Bodenstein and Lind (A., 1907, ii, 76) on the formation of hydrogen bromide that the reaction occurs as a result of the following changes: $\text{Br} + \text{H}_2 = \text{HBr} + \text{H}$ (primary reaction) and $\text{H} + \text{Br}_2 = \text{HBr} + \text{Br}$ or $\text{H} + \text{HBr} = \text{H}_2 + \text{Br}$, and consequently the dissociation of hydrogen bromide takes place with the reaction $\text{Br} + \text{HBr} = \text{Br}_2 + \text{H}$ as the primary change, and is followed by the same secondary reactions as above. It is also shown that the existing experimental data do not exclude the possibility of the formation and dissociation of hydrogen iodide according to the same scheme. The numerical results of Bodenstein and Lind have been used to calculate the critical energy of the process $\text{Br} + \text{HBr} = \text{Br}_2 + \text{H}$ and the value 43,700 cal. obtained. The results are generally considered, and it is concluded that in respect of the heat of dissociation of hydrogen, Langmuir's value, 84,000 cal. (A., 1915, ii, 249), is probably not irreconcilable with Bohr's theoretical value, 62,000 cal. (A., 1913, ii, 1045). A method of illustrating the above-mentioned reaction by means of models of atoms and molecules similar to those of Bohr is indicated. J. F. S.

Periodic Acid and Periodates. ARTHUR ROSENHEIM and ELSE LOEWENTHAL (*Kolloid. Zeitsch.*, 1919, 25, 53–60).—The periodates of sodium, lithium, ammonium, and guanidine have been investigated. The hydrogen-ion concentration of *N*/20-solutions of H_5IO_6 , NaH_4IO_6 , and $\text{Na}_2\text{H}_3\text{IO}_6$ was determined by Sørensen's indicator method with the object of finding the most suitable indicator for use in titrating periodic acid with sodium hydroxide. The hydrogen-ion concentrations found are respectively 6×10^{-3} , 4.05×10^{-7} , and 6.5×10^{-10} . It is shown that, using methyl-orange as indicator, periodic acid can be quantitatively converted by titration into NaH_4IO_6 , and that using thymolphthalein as indicator it is converted into $\text{Na}_2\text{H}_3\text{IO}_6$. The solubility of $\text{Na}_2\text{H}_3\text{IO}_6$ is determined at various temperatures, and the following values in grams per 100 grams of solution obtained: 0°, 0.104; 25°, 0.157; 40°, 0.187; 100°, 0.434. Shaking with 10*N*-sodium hydroxide solution converted this salt into $\text{Na}_3\text{H}_2\text{IO}_6$. A number of experiments, designed to ascertain whether the sodium periodates adsorb sodium hydroxide, were carried out at 17° by shaking periodic acid with a concentrated solution of sodium hydroxide. The experiments show that neither of the sodium periodates mentioned exhibit any colloidal properties, and that these are the only sodium periodates capable of existence in aqueous solution. On the addition of 1 mol. of periodic acid to 2 mols. lithium hydroxide solution a white precipitate is formed which immediately dissolves; the solution, on warming, yields a

white precipitate consisting of microscopic spherules, which on analysis is shown to consist of $\text{Li}_3\text{H}_2\text{IO}_6$. The mother liquor on keeping deposits small, white, six-sided bipyramids of $\text{Li}_2\text{H}_3\text{IO}_6$. Attempts to prepare LiIO_4 and Li_5IO_6 , compounds described by Rammelsberg, failed. The two lithium salts were examined as to the power of adsorption as in the case of the sodium salts, and it is shown that absorption compounds are formed up to the ratio $\text{Li}_2\text{O}/\text{I}_2\text{O}_7 = 5.39$. The two ammonium periodates $(\text{NH}_4)_2\text{H}_3\text{IO}_6$ and NH_4IO_4 previously described by Rammelsberg (*Ann. Phys. Chem.*, 1868, **134**, 379) were obtained, and a further compound, $(\text{NH}_4)_5\text{H}_7(\text{IO}_6)_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$, was also obtained. The last compound was prepared in rectangular crystals by shaking periodic acid with an excess of 25% ammonia at 140° for several hours. Two guanidine periodates, $(\text{CN}_3\text{H}_6)_3\text{H}_2\text{IO}_6$ and $(\text{CN}_3\text{H}_6)_2\text{H}_3\text{IO}_6$, were obtained by treating periodic acid with guanidine. Both substances are very sparingly soluble, white, crystalline compounds. The molecular conductivity, boiling point, and freezing point of a number of solutions of periodic acid have been determined. The conductivity determinations show that periodic acid is of medium strength, whilst the boiling-point determinations indicate that it dissociates into two ions, and the freezing-point determinations show that a 5% solution is much less dissociated, and that in a 12–20% solution polymeric periodic acid molecules are present. In general, the work shows that there is a decided, if not very far-reaching, analogy between periodic acid and the periodates on the one hand and telluric acid and the tellurates on the other.

J. F. S.

Flame Reactions of Selenium and Tellurium. HARRY B. WEISER and ALLEN GARRISON (*J. Physical Chem.*, 1919, **23**, 478–497. Compare A., 1914, ii, 317, 398; also Papish, this vol., ii, 105).—The luminescence and the nature of the deposits produced when selenium and tellurium are introduced into various flames have been experimentally examined. The flames used were: air-hydrogen, bunsen, hydrogen-air, and chlorine-hydrogen; the effect of cathode rays on sulphur, selenium, and tellurium was also examined. It is shown that the reaction from selenium to selenic salt produces a blue luminescence, which is the most characteristic in flames containing selenium. It is probable that this luminescence is due chiefly to the reaction from selenic ion to unionised selenic salt. The reaction from tellurium to tellurous salt produces a green luminescence; and from tellurous salt to telluric salt a blue luminescence. It is probable that the green luminescence is due chiefly to the reaction from tellurous ion to the unionised tellurous salt; and the blue luminescence from telluric ion to the undissociated telluric salt. Under certain conditions a red luminescence occurs in flames containing selenium, which is, as a rule, less intense than the blue luminescence. Since the vapours of both elements are coloured, it is probable that the red coloration in both cases is due in part to the colour of the vapours, in part to a purely thermal luminescence, and in part to some stage of the chemical reaction from the vapour of the element to the quadrivalent ion. A green

tip in the flames in air charged with selenium and tellurium compounds is not a luminescence, but is due to the green colour of the vapour of the dioxide, which appears greener by reflecting the blue luminescence just below.

J. F. S.

The Determination of the Rate of Solution of Atmospheric Nitrogen and Oxygen by Water. II. W. E. ADENEY and H. G. BECKER (*Sci. Proc. Roy. Dublin Soc.*, 1919, **15**, 609—628).—The work previously recorded (compare this vol., ii, 104) has been continued with the object of reducing the observations to unit area and volume, and has been extended to include oxygen and nitrogen as pure gases. The apparatus used has also been modified so as to obtain a better temperature control and to eliminate any errors arising from the temperature and vapour pressure of the replenishing gas. A formula is given in each case for oxygen, nitrogen, and air, from which it is possible to calculate the rate of solution of the gas dealt with for any conditions of area exposed, depth, or degree of saturation, provided that the water is kept uniformly mixed.

W. G.

Triatomic Nitrogen, N_3 . MAX TRAUTZ (*Zeitsch. Elektrochem.*, 1919, **25**, 297—300).—A mathematical paper, in which it is shown that at all temperatures above that of liquid air the predominating constituent of active nitrogen (Strutt, T., 1918, **113**, 200) is triatomic nitrogen, N_3 . The concentration of this substance in active nitrogen is represented by its partial pressure, 0.002 mm. The heat of formation from N_2 and N has a maximum value of 5000—10,000 cal. It is therefore, at ordinary temperatures, so much more stable than a mixture of N_2 and N that the decomposition $N_3 + N = 2N_2$ increases because of the relatively large increase in the concentration of triatomic nitrogen with falling temperature. In this fact the irregular temperature-coefficient finds its meaning. Since the cooling of active nitrogen by liquid air does not occur instantaneously, the triatomic nitrogen and the trimolecular destruction of active nitrogen, at temperatures above that of liquid air, predominate over the monatomic nitrogen and its binary compound N_2 . The velocity constant of the third order is of the dimension 10^{17} mol./c.c. as a maximum, and can be much smaller if the third order reaction predominates only at ordinary temperatures. The deactivating of active nitrogen with falling temperature may either pass through a minimum or it may reach a maximum, $k/K = 10^{36}$, which is in keeping with the very large inverse of the temperature-coefficient. Where the triatomic nitrogen preponderates over the monatomic nitrogen at low temperatures above that of liquid air, hexatomic nitrogen must of necessity be formed in the mixture, in quantities which are very small compared with the triatomic nitrogen. The small heat of formation of triatomic nitrogen which is deducible from the very large reaction velocity and is in keeping with the inefficual attempts to prepare it pure, indicates that it is impossible to prepare this substance pure by thermal methods alone. For on cooling it reacts with monatomic nitrogen to form diatomic nitrogen, and on warm-

ing it decomposes into monatomic nitrogen and hexatomic nitrogen. It is extremely probable that triatomic nitrogen is an open-chain molecule, and that similar triatomic molecules of oxygen, chlorine, bromine, and iodine can also exist, whilst a similar hydrogen molecule cannot exist. The open-chain structure for triatomic nitrogen is indicated by the nitride formation and by the absence of azide formation. The triatomic oxygen will be an isomeride of ozone.

J. F. S.

The Discovery of Phosphorus Two Hundred and Fifty Years Ago. HERMANN PETERS (*Prometheus*, 1919, 30, 249—251, 259—261; from *Chem. Zentr.*, 1919, iii, 111).—Evidence is adduced to show that Hennig Brand is the sole discoverer of phosphorus, and that the rapid spread of the knowledge of the method of preparation is due to Leibniz. The discovery was made in 1669. The application of phosphorus to technical purposes was hindered at first by its high price. The latter was greatly reduced about a hundred years later, when phosphorus was extracted from bone ash by P. Gahn and Scheele. The first phosphorus matches, the so-called Turin candles, were introduced into commerce at the end of the eighteenth century. At the beginning of the nineteenth century the first phosphorus-sulphur matches were made on a small scale, but the actual production of phosphorus matches dates from about 1833. Johann Kunckel's claim of the independent discovery of phosphorus is unfounded, and was disputed by Leibniz. H. W.

Separation by Solidification of Pure Carbon Dioxide from a Gaseous Mixture. V. CRÉMIEU and A. LEPAPE (*Compt. rend.*, 1919, 169, 654—655).—Carbon dioxide may be obtained in a pure, solid state from a gaseous mixture rich in that gas either by allowing the compressed gas to expand suddenly from a narrow orifice through a cloth bag into the air or by compressing the mixture slightly in a vessel cooled to -80° . The solid carbon dioxide is, in either case, free from radium emanation when the latter is present in the original mixture. W. G.

The Effect of Sea-salt on the Pressure of Carbon Dioxide and Alkalinity of Natural Waters. EDMUND BRYDGES RUDHALL PRIDEAUX (*T.*, 1919, 115, 1223—1230).

The Solubility of the Inert Gases in Liquids. ANDREAS VON ANTROPOFF (*Zeitsch. Elektrochem.*, 1919, 25, 269—297).—The solubility of helium, argon, neon, krypton, and xenon has been determined in water at various temperatures, and the solubility of krypton has been determined in pentane, acetic acid, and aniline. Several pieces of apparatus are described which are specially designed for working with the inactive gases. These include (1) a simplified and improved form of the Toepler mercury pump; (2) an absorption pipette, which enables an absorbing liquid or solution to be introduced into a gas contained over mercury, and to be withdrawn again without loss of gas; (3) an apparatus for solubility deter-

minations, in which neither the liquid nor its vapour comes into contact with taps, and (4) a burette in which the gas can be expelled from solution, and which allows of a definite amount of liquid being introduced into the solubility apparatus. The original should be consulted for details and dimensions of the apparatus. The helium used in the experiments was obtained by heating cleveite at 1000° in a porcelain tube, and the product purified in the usual way. The following solubilities (β) in water were obtained: 0°, 0·00967; 10°, 0·00991; 20°, 0·00996; 30°, 0·01007; 40°, 0·01029; 50°, 0·0108. These figures are about 40% smaller than the values found by Estreicher (A., 1900, ii, 205). Argon, krypton, and xenon were separated by a method similar to that of Ramsay and Moore (T., 1908, **93**, 2181). The following solubility values in water were obtained: Neon, 0°, 0·0114; 10°, 0·0118; 20°, 0·0147; 30°, 0·0155; 40°, 0·0217; 50°, 0·0322. Krypton, 0°, 0·1095; 10°, 0·0807; 20°, 0·0626; 30°, 0·0511; 40°, 0·0433; 50°, 0·0383; 60°, 0·0357. Xenon, 0°, 0·2200; 10°, 0·1580; 20°, 0·1109; 30°, 0·0893; 40°, 0·0745; 45·45°, 0·0663. In pentane, xenon has the following absorption coefficients: 11·7°, 0·1686; 20°, 0·1335; 25°, 0·1272; 30°, 0·1009; 40°, 0·0949; 49·5°, 0·1084; in aniline, the solubilities per gram are: 10°, 0·6687; 20°, 0·5006; 30°, 0·4426; 40°, 0·4336; 50°, 0·3892. The solubility of the inert gases in water increases with the molecular weight, and in the case of the heavier gases, niton, xenon, krypton, and argon, decreases with increasing temperature. The solubility of helium is practically independent of temperature, whilst that of neon increases rapidly with increasing temperature.

J. F. S.

Solubility of Calcite in Sea-water in Contact with the Atmosphere and its Variation with Temperature.

ROGER C. WELLS (*Carnegie Inst. Publication*, 1918, No. 213 [*Papers from Dept. Marine Biology*, **9**, 316—318]).—Certain equilibria, the attainment of which would be expected from experiments in the laboratory, do not seem to be fully attained under natural conditions in the ocean. The equilibria referred to involve the effect of temperature on the exchange of carbon dioxide between sea-water and the atmosphere and the precipitation or solution, as the case may be, of various solid constituents from or into sea-water. Apparently the adjustments occur so slowly, and the bulk of the ocean is so great, with reference to the surface exposed to the atmosphere, that the expected variations with temperature do not appear in the water of the open ocean. Sea-water in contact with an excess of calcite was agitated by a current of outdoor air for forty days, and the dissolved carbonates were estimated at intervals by titration with 0·02*N*-sodium hydrogen sulphate, using methyl-orange as an indicator. Experiments were made at 1° and at the ordinary temperature (25° to 29°). The colder sea-water tended to retain more carbonate in solution than warmer sea-water, but did not dissolve fresh calcite. Ordinary sea-water appears to contain so much carbonate that in contact with the atmosphere at 1° it

neither has nor acquires an appreciable solvent action on calcite. At higher temperatures, it undergoes a slow diminution in its content of carbonates on being agitated in contact with outdoor air.

CHEMICAL ABSTRACTS.

Gravitational Attraction and Uranium-Lead. ANDERS BULL (*Science*, 1919, **50**, 69—70).—No one has satisfactorily explained the discrepancies between the atomic weight of ordinary lead and that of lead from uranium minerals. It is suggested that a difference may exist in their behaviour towards the force of gravitation. Deviations in the value of gravitational acceleration might be proportional to variations in their atomic weight, which would make the atomic mass of all kinds of lead identical. Assuming, finally, that the gravitational attraction is due to electrons, variations in atomic weight might be ascribed to electronic tension set up in the atom by radioactive disintegration and gradually diminishing in the end-product of the series.

CHEMICAL ABSTRACTS.

Critical Study of the Potassium and Sodium Double Salts of Lead Tetrafluoride as Sources of Fluorine.

GEORGE L. CLARK (*J. Amer. Chem. Soc.*, 1919, **41**, 1477—1491).—An investigation of the methods of preparation and properties of the double salts formed by lead tetrafluoride with sodium and potassium fluoride respectively, with the object of finding a suitable substance for the preparation of fluorine. *Tripotassium lead hydrogen octafluoride*, $3\text{KF}\cdot\text{HF}\cdot\text{PbF}_4$, is prepared by adding potassium plumbate in small quantities to a concentrated aqueous solution of hydrofluoric acid until a separation of lead dioxide occurs. The solution is filtered through paper supported by several layers of cloth, and the filtrate evaporated slowly in lead dishes on a sand-bath in a gentle current of air until a separation of crystals occurs. The solubility of this salt has been determined in the presence of hydrofluoric acid and potassium fluoride. In the absence of acid, hydrolysis occurs, with the separation of lead dioxide. When heated at 250° , the hydrogen fluoride molecule is expelled, and at temperatures above 250° fluorine is driven off. *Potassium plumbate*, $\text{K}_2\text{PbO}_3\cdot 3\text{H}_2\text{O}$, is best prepared by mixing three molecules of potassium hydroxide with 20% of its weight of water, raising the temperature to 100° , and adding one molecule of lead dioxide; action at once occurs, and the plumbate is formed without decomposition products. This salt is regarded as the dipotassium salt of orthoplumbic acid, $\text{K}_2\text{Pb}(\text{OH})_6$, and, on treatment with water, hydrolyses according to the equations

$$\text{K}_2\text{Pb}(\text{OH})_6 + 2\text{H}_2\text{O} \rightleftharpoons 2\text{KOH} + \text{H}_2\text{Pb}(\text{OH})_6,$$
$$\text{H}_2\text{Pb}(\text{OH})_6 = \text{H}_4\text{PbO}_4 + 2\text{H}_2\text{O}.$$
 In the presence of 20% of water, the hydrolysis proceeds so far that hydrated lead dioxide is precipitated. *Sodium lead hexafluoride*, $2\text{NaF}\cdot\text{PbF}_4$, is prepared by the addition of sodium plumbate to aqueous hydrofluoric acid, and crystallisation of the product from hydrofluoric acid to separate sodium hydrogen fluoride. The crystals occur in stout, short plates

which are hydrolysed by water. The solubility has been determined in water containing hydrofluoric acid and sodium fluoride, and is shown to decrease with increasing concentration of hydrogen fluoride until sodium hydrogen fluoride is formed, and then it increases in solubility with an increase in the concentration of hydrogen fluoride. This salt liberates fluorine at 250° . *Sodium plumbate*, $\text{Na}_2\text{PbO}_3 \cdot 6\text{H}_2\text{O}$, is prepared by mixing 150 grams of sodium hydroxide with 50 c.c. of water at 100° , adding lead dioxide until a paste is formed, then adding 25 c.c. of water and lead dioxide to make a total quantity of 300 grams of the latter substance. This salt is much less stable and more easily hydrolysed than the potassium salt. The analysis of the double fluorides is effected in the following manner. The salt is dissolved in water, when hydrolysis occurs, thus: $2(3\text{KF} \cdot \text{HF} \cdot \text{PbF}_4) + 4\text{H}_2\text{O} = 6\text{KF} + 10\text{HF} + 2\text{PbO}_2$; the lead dioxide is filtered off in an alundum crucible, dried at 105° , and weighed. The filtrate is made up to a known volume; in one portion, the free acid is estimated by titration, and in another the potassium fluoride is estimated by evaporation to dryness and ignition at 500° . The two double fluorides are considered as sources of fluorine. The potassium salt is more easily prepared and is more stable than the sodium salt, and, weight for weight of materials used, the potassium salt is twice as efficient as the sodium salt.

J. F. S.

Colloidal Tricalcium Aluminate. A. J. PHILLIPS (*J. Amer. Ceram. Soc.*, 1919, **2**, 708—742).—Pure amorphous, calcined, and finely ground tricalcium aluminate forms a true colloidal sol in water, an insignificant proportion of the substance entering into true solution. The crystalline form appears to be highly polymerised, and in contact with water behaves like a colloid, but if suspension is incomplete, the residue may consist of hydrated crystals. A more concentrated suspension is obtained by using lime-water instead of pure water, and the product does not diffuse or dialyse, shows the Tyndall cone, is positively charged, is not coagulated by heat, but is coagulated by freezing, has a high adsorptive power, and generally resembles the well-known sols of ferric, aluminium, and chromic oxides. It does not form a gel on evaporation or by dehydration over sulphuric acid, the product in each case being a loose powder. The lime:alumina ratio in the filtered suspensions never corresponded with $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, lime always being deficient, but to an irregular extent, varying with the time, from 1:1.096 after three hours to 1:1.519 after twenty-eight days. The deficiency in the lime is attributed to the free lime being adsorbed by the colloidal aluminate.

The colloidal aluminate is an anhydride which, by capillary attraction, endosmose and molecular imbibition, swells, forming an emulsoid. On the first addition of water to the aluminate, there is a development of heat—due to the formation of an exothermic hydrate. The aluminate is more soluble in cold than in hot water, so that if it is first exposed to moist air and then mixed with water, the conditions favour a great concentration of aluminate in true

solution, this being accompanied by an endothermic change. There is a further development of heat resulting from the disturbance of the equilibrium $(H_2O)_n \rightleftharpoons nH_2O$ of the water-molecules. This is also eliminated when the aluminate has previously been exposed to moist air. When there is a sufficient concentration of cations to disperse the hydrated aluminate as fast as it is formed, the resultant heat effects are either zero or negative, as this dispersion is accompanied by an absorption of heat. The treatment of the colloidal gel only changes the composition of the outer surface; any ionic activity is confined to the surface, except when the film is ruptured, and is a characteristic adsorption effect.

A greater dispersion of aluminate occurs in lime-water than in pure water, as the calcium ions of the calcium hydrate are adsorbed more than the hydroxyl ions by the hydrated aluminate, and when a sufficient number of ions has been adsorbed, their charges and those of the aluminate repel each other, and the aluminate is thereby dispersed.

Any water adsorbed is compressed in the process, any salts in solution being similarly compressed, and their solubility is increased.

As the aluminate can only adsorb a limited amount of cations, when the concentration of the anions is sufficiently increased, the positive charges on the aluminate will be neutralised by the adsorption of the anions because of their increased concentration, and uncharged aluminate is precipitated. The adsorbing surface is decreased, and the ions previously held by adsorption are returned to the solution and exercise a dispersive effect on undispersed material. Hence the concentration of negative ions is greatly increased. A much weaker solution of sodium hydroxide shows the same precipitating effect.

When a smaller amount of water is used, as in preparing cement pastes, the aluminate is converted into a colloidal gel which persists for at least twenty-four hours. On continuing the mixing of the aluminate and water for several minutes, a considerable retardation occurred in the time of setting, but by increasing the percentage of hydrate, so that the total ion-concentration exceeded the adsorptive capacity of the aluminate for cations, the time of setting was reduced. A semipermeable film is formed around the grains of aluminate, which is destroyed on mechanical agitation, a sol being formed at the same time.

On stirring a mixture of equal weights of the aluminate and water, and then slowly adding a volume of hydrochloric acid (D 1.21) equal to that of the water, continuing the stirring and keeping the vessel cool, the viscous paste soon solidifies, and, on keeping, synothesis occurs, an aqueous layer separates, and solidifies to a clear gel containing both alumina and lime.

The rate of coagulation of the aluminate gel is thus affected by the amount of dispersion effected, the synothesis of the gel, the neutralisation of previously adsorbed calcium ions by hydroxyl ions, and the adsorption of undissociated salt. [See also *J. Soc. Chem. Ind.*, 1919, 904A.]

A. B. S.

Rôle of Water of Crystallisation and the Structure of Alums. CLEMENS SCHAEFER and MARTHA SCHUBERT (*Ann. Physik*, 1919, [iv], **59**, 583—588).—Polemical. It is shown that the crystal model of alum put forward by Vegard and Schjelderup is not correct (A., 1918, ii, 156). It is maintained that the rôle allotted to the water of crystallisation in the crystalline structure of alums by Vegard was put forward by the present authors two years previously (A., 1916, ii, 505). The authors therefore claim priority in this matter. J. F. S.

Amalgams. II. Colloidal Gold Amalgam. C. PAAL and HERMANN STEYER (*Kolloid Zeitsch.*, 1919, **25**, 21—26. Compare this vol., ii, 69).—The gold amalgam sol previously described, on keeping, is oxidised to some extent by atmospheric air; this partly oxidised sol has a somewhat browner solution than the sol when freshly prepared, but may be brought back to its original colour by the addition of a few drops of hydrazine hydrate solution. A small quantity of the sol was kept in solution for twenty-two weeks with the object of determining its stability. It was found that the colour became more fiery-red and that a heavy, grey gel separated. The remaining solid was dried in a vacuum and gave a blackish-violet substance, which was in the form of lamellæ with a bronze tinge; it was completely soluble in water, and had the composition $\text{AuHg}_{0.34}$. The gel contained 5.32% of lysalbic acid, which was used as a protecting colloid, and had the composition $\text{AuHg}_{0.9}$. The gel was non-reversible on warming with either sodium hydroxide or ammonia solution. A number of other experiments are described on the stability of the colloid. J. F. S.

Mineralogical Chemistry.

A Lead-grey, Fibrous Mineral from Binn, Switzerland.

R. H. SOLLY. With a chemical analysis by G. T. PRIOR (*Min. Mag.*, 1919, **18**, 360—362).—Fine, acicular crystals associated with seligmannite, and sometimes grouped as triangular lattices in cavities of the dolomite, resemble in their cleavage, colour, and chocolate-coloured streak the several thioarsenites of lead (liveingite, rathite, baumhauerite, and dufrenoyite) found at this locality. Goniometric measurements in the prism-zone, the only one developed, accord more closely with the angles of dufrenoyite, whilst the analysis corresponds with rathite, $3\text{PbS}, 2\text{Sb}_2\text{S}_3$. The presence of thallium is of interest (compare A., 1918, ii, 323).

Pb.	Ag.	Cu.	Th.	Fe.	As.	Sb.	S.	Insol.	Total	D ₄ ¹⁸ .
51.11	0.76	0.10	0.23	0.21	23.37	0.74	23.22	0.24	99.98	5.453

L. J. S.

Semseyite from Dumfriesshire. G. F. HERBERT SMITH. With a chemical analysis by G. T. PRIOR (*Min. Mag.*, 1919, **18**, 354—359).—Specimens of ore from the old antimony-lead mine at Glendinning in Eskdale show small cavities with a drusy lining of minute, iron-black crystals of a thioantimonite of lead. The associated minerals are stibnite, valentinite, ankerite, calcite, blende, and pyrites. The crystals are monoclinic with constants ($a:b:c=1.1356:1:1.0218$, $\beta=74^\circ 14'$) somewhat different from those previously determined for pligionite and semseyite; but the following analysis of the drusy lining, together with the underlying massive material, agree with the semseyite formula, $9\text{PbS}, 4\text{Sb}_2\text{S}_3$.

Pb.	Sb.	S.	Fe.	Zn.	CaCO_3 .	MgCO_3 .	Insol.	Total.	Sp. gr.
52.37	25.49	18.81	0.67	trace	1.66	trace	0.81	99.81	5.84

L. J. S.

Ferrazite, a New Associate of the Diamond. T. H. LEE and LUIZ FLORES DE MORAES (*Amer. J. Sci.*, 1919, [iv], **48**, 353—354).—Some dark yellowish-white pebbles ("favas") from the Brazilian diamond deposits gave the following results on analysis. After deducting silica and alumina as kaolinite and wavellite, the formula is $3(\text{Pb}, \text{Ba})\text{O}, \text{P}_2\text{O}_5, 8\text{H}_2\text{O}$. Thin sections under the microscope show a granular structure, D 3.0—3.3:

PbO.	BaO.	CaO.	Al_2O_3 .	P_2O_5 .	SiO_2 .	H_2O .	Total.
45.63	8.87	trace	3.48	26.24	2.44	14.20	100.86

L. J. S.

Crystallography of Vogtite, an Anorthic Metasilicate of Iron, Calcium, Manganese, and Magnesium, from Acid Steel-furnace Slags. A. F. HALLIMOND (*Min. Mag.*, 1919, **18**, 368—372).—Acid steel-furnace slags consisting mainly of FeO , MnO , and SiO_2 yield the silicates fayalite and rhodonite; but when the amount of lime exceeds about 8% the new silicate *vogtite* separates as long, blade-like crystals. The composition of these is given under I, agreeing approximately with $(\text{Fe}, \text{Ca}, \text{Mn}, \text{Mg})\text{SiO}_3$; II gives the composition of the slag. The crystals are anorthic, $a:b:c=1.093:1:0.729$, $\alpha=99^\circ 37'$, $\beta=99^\circ 21'$, $\gamma=83^\circ 53'$, with perfect cleavages parallel to $M(\bar{1}10)$ and $m(110)$. Optical determinations are given; $\beta=1.701$, $2V_D=65\frac{1}{2}^\circ$, optically negative. The crystals, when free from included glass, are transparent and pale amber-yellow in colour:

	SiO_2 .	Al_2O_3 .	Fe_2O_3 .	FeO .	MnO .	CaO .	MgO .	TiO_2 .	Total.	Sp. gr.
I.....	47.4	0.15	2.7	15.95	12.95	15.1	5.26	0.10	99.61	3.39
II.....	47.9	1.72	1.2	20.85	10.8	13.0	3.89	0.58	99.4	—

Vogtite differs in density and optical orientation from pyroxmanigite (A., 1913, ii, 869) and sobralite (this vol., ii, 165). L. J. S.

The Role of Boron in Silicates G. CESARO (*Riv. Min. Crist., Ital.*, 1918, **50**, 3—31).—The compositions of borosilicate minerals are discussed, and it is shown that in every case the function of boron is best explained as that of an acid. Datolite is accordingly

an acid metasilicate of calcium, with some silicon replaced by " (B_2O) ." Homilite is similar, containing also iron. Euclase corresponds with datolite with aluminium instead of boron, and glucinum instead of calcium. A table is given showing the existence in minerals of acids of boron corresponding with each of those of silicon. Axinite is a combination of di-ortho- and meta-silicates, or a basic triple metasilicate, with B_2O replacements. Tourmaline is an orthosilicate with part of the silicon replaced by B_2O . Danburite is a neutral tricalcium metasilicoborate. Howlite is an orthosilicate, with replacement. In addition to these, the natural borates can be expressed by structural formulæ. The possible constituents of boron acids are discussed.

CHEMICAL ABSTRACTS.

Analytical Chemistry.

Tincture of Muscari as an Indicator. E. DUFILHO (*Bull. Soc. Pharm., Bordeaux*, 1918, **4**, 202; from *Ann. Chim. anal.*, 1919, [ii], **1**, 325—326).—An alcoholic extract of muscari flowers (grape-hyacinth) may be used as an indicator in acidimetry, the colour change being from red in acid solution to green in alkaline solution. It behaves like litmus in the case of mineral acids, oxalic acid, alkalis and ammonia, and like methyl-orange with phosphoric acid; it is not affected by boric acid except in the presence of glycerol.
W. P. S.

Coloured Indicator Papers. I. M. KOLTHOFF (*Pharm. Weekblad*, 1919, **56**, 175—187).—An examination of the sensitiveness of indicator papers with reference to the quality of the paper itself and its pre-treatment with acid, alkali, or aluminium hydroxide; the nature of the colouring matter used, and its concentration on the paper. Sized papers are less sensitive than unsized, although the reaction on the former is sharper. Otherwise the kind of paper used, and any previous treatment it may have had, are of little importance. The most sensitive Congo paper was obtained by treating filter paper with a 0.1% solution of the dye. This indicated an acidity of 0.0001*N*-hydrochloric acid. The most sensitive paper for strong acids and bases is prepared from a 0.1% solution of azo-litmin.
W. S. M.

Titration of Acids by the Conductivity Method. P. A. MEERBURG (*Chem. Weekblad*, 1919, **16**, 1338—1347).—In the titration of various acids with alkalis the author has determined the neutralisation point by a conductivity method. If a graph is plotted in which the abscissæ are represented by c.c. of 0.86*N*-sodium

hydroxide and the ordinates by the values $(1000 - a)/a$, the neutralisation point will be indicated by a definite bend in the curve. With a strong acid and base this bend will be sharp, but it will be obtuse in the case of a weak acid and strong base. With acids and bases having a dissociation-constant, $K > 10^{-10}$, the neutralisation point is readily determined (Dutoit and Duboux, "L'analyse des vins par volumétrie physico-chimique," 54), but if hydrolysable salts are formed the curve becomes continuous and the neutralisation point is masked. In titrating a mixture of two acids having widely differing degrees of ionisation, for example, hydrochloric acid and phenol, the neutralisation of the hydrochloric acid takes place first and is indicated by the lowest portion of the curve, a sharp bend then denoting the neutralisation of the phenol. When the acids have the same ionising power, the method fails, as the lowest point on the curve cannot be accurately determined. Accurate results are obtainable in cases where the relative proportions of the stronger acid to the weaker are 1:1 or 1:2.5, but when the proportions were 2.5:1 the author found the results too low for the strong acid and too high for the weaker one. Tables and curves are given for various acids, such as hydrochloric acid, oxalic acid, lactic acid, and mixtures of these. The method is suitable for the estimation of small amounts of acidity, as, for example, in chyle. W. J. W.

The Amalgamated Copper Cathode in Electro-analysis.

JOSÉ ALEMANY Y SELFA (*Anal. Fis. Quim.*, 1919, 17, 174—188).—The advantages in the use of mercury as cathode material in the electrolytic precipitation of metals are neutralised to some extent by the difficulties of manipulation. These difficulties are obviated by the use of the amalgamated electrode described. The cathode is of copper gauze, 5.5 × 11 cm. On this is deposited about 1 gram of silver by electrolysis in alkaline silver cyanide solution. The cathode is then amalgamated by electrolysis in mercurous nitrate solution until 0.8—1.5 gram of mercury has been deposited. It is then washed with water, alcohol, and ether. In combination with this cathode a rotating anode of platinum or of iron is employed. The temperature of electrolysis must not exceed 45°. A detailed account of the following electrolytic estimations is given: zinc in alkaline, ammoniacal, and neutral solution in presence of nitrate; zinc in sulphuric acid solution; cadmium in ammoniacal solution in presence of nitrate; cadmium in sulphuric acid and in neutral solution. In all cases the results obtained were excellent. W. S. M.

Graphic Representation of the Chemical Composition of Natural Waters. ENRIQUE HERRERO DUCLOUX (*Anal. Fis. Quim.*, 1917, 15, 477—483).—The analytical results are graphically represented in relation to a regular hexagon of reference. The amounts of the six commonly occurring cations, Fe''' , Al''' , Ca'' , Mg'' , K' , Na' , are measured off in an invariable order along the six axes radiating from the centre of the hexagon through the vertices and the points thus marked off are joined. The six anions, SiO_3'' , SO_4'' , HCO_3' , Cl' , NO_3' , HS' , are similarly treated. The chemical

composition of the water is completely represented by the two irregular hexagonal figures so formed. W. S. M.

Chemical Analysis with Membrane Filters. RICHARD ZSIGMONDY and GERHART JANDER (*Zeitsch. anal. Chim.*, 1919, **58**, 241—280).—The membrane filters described by Zsigmondy and Bachmann (A., 1918, ii, 307) may be used generally in analysis; the filtration is rapid, the precipitate is washed readily, and very fine crystalline or colloidal precipitates are retained completely by the filters. The membrane is mounted for use in the apparatus (flanged funnel, perforated disc and ring) described previously by Zsigmondy (A., 1913, ii, 857). W. P. S.

Estimation of Small Quantities of Alkali Iodides in the Presence of Bromides and Nitrites. ED. LASAUSSE (*J. Pharm. Chim.*, 1919, [vii], **20**, 177—181).—The nitrite is oxidised by potassium permanganate in phosphoric acid solution at 40°; sodium hydrogen sulphite is then added to reduce chlorates and bromates, and the solution is boiled with the addition of potassium hydroxide and potassium permanganate; the iodide is thus converted into iodate, whilst the chloride and bromide are not affected. The iodate is then determined iodometrically. [See, further, *J. Soc. Chem. Ind.*, 1919, 899A.] W. P. S.

Estimation of Iodine in Cuprous Iodide. ED. LASAUSSE (*J. Pharm. Chim.*, 1919, [vii], **20**, 181—183).—Two methods are described. In the first, the cuprous iodide is decomposed with ferric chloride solution, the liberated iodine dissolved in carbon disulphide, and the solution separated and titrated. In the second method, the cuprous iodide is boiled with potassium hydroxide solution, and the resulting potassium iodide estimated in the solution by oxidation to iodate by means of potassium permanganate in alkaline solution, as described in the preceding abstract. [See, further, *J. Soc. Chem. Ind.*, 1919, 899A.] W. P. S.

Modified Benedict Method for the Estimation of Sulphur in Feeds, Faeces, and Foods. J. O. HALVERSON (*J. Amer. Chem. Soc.*, 1919, **41**, 1494—1503).—The following modified Benedict method for the estimation of sulphur in foods and faeces is described. About 3·44 grams of faeces or 2·7476 grams of cattle food are rolled up in half a filter paper and placed in a 300 c.c. Kjeldahl flask. Ten to fifteen c.c. of hot water are added, and the flask heated on a steam-bath with slight shaking, 20 c.c. of a mixture of concentrated and fuming nitric acid (1:4) are added, the flask stoppered with a small funnel, and kept for twelve hours. It is then placed on a steam-bath and digested for four days with occasional shaking. At the end of that time, a further 10 c.c. of the acid mixture are added, and the digestion continued until the solution is clear, when it is transferred in portions to a 60 c.c. evaporating basin and treated with 20 c.c. of the Benedict reagent during evaporation to complete dryness on the steam-bath. It is

then slowly baked on a sand-bath. The blackened residue is heated until it fuses, and then the temperature is lowered so that it solidifies slowly. About 20 c.c. of (1:4) hydrochloric acid are added, and the mixture heated for fifteen minutes on the steam-bath. The clear solution is then filtered into a 250 c.c. beaker, made up to 100 c.c. with water, heated to boiling, and treated with 10 c.c. of boiling 5% barium chloride solution from a dropper; the addition should take four minutes. The precipitate is digested for two to three hours on a hot plate, and then kept cold for forty-eight hours and filtered. It is shown that when silica is present, the peroxide method has a tendency to give high results. When the silica is removed, the results agree with those of the Benedict method to the third decimal place.

J. F. S.

Gravimetric Estimation of Sulphate as Barium Sulphate.

I. M. KOLTHOFF and E. H. VOGELZANG (*Pharm. Weekblad*, 1919, **56**, 122—142).—A detailed investigation into the sources of error in the estimation of sulphate as barium sulphate. The solubility of barium sulphate is increased by the addition of acids or of salts, except in the case where barium ion or sulphate ion is supplied. Samples of barium sulphate prepared in various ways show differences in solubility depending chiefly on the size of the particles. The solubility in water at ordinary temperatures is negligible. The solubility figures obtained in hydrochloric acid solution for acid concentrations $N/1$, $N/2$, $N/10$ are, respectively, 54, 31, and 11 mg. per litre. At 90° , the solubilities in $N/1$, $N/2$, and $N/20$ -acid were 416, 265, and 77 mg. per litre respectively.

In the estimation, reduction of barium sulphate during ignition of the dry precipitate and filter was found to take place to a slight extent in a porcelain crucible, and to a considerable extent in platinum. This can be avoided by ignition of the moist filter. Simultaneous precipitation of other salts with barium sulphate is caused by: (1) "conglomerate formation"; (2) solid solution; (3) adsorption; (4) mixed crystals; (5) mechanical inclusion; (6) chemical reaction. With regard to (2) and (3), experiments showed that in acid solution barium sulphate did not absorb electrolytes; (4) is an improbable case, as the commonly occurring salts in the precipitation belong to a different crystallographic group. Impurities in the barium sulphate are accounted for chiefly by the reactions between the SO_4^{--} ion and the intermediate ions of other salts (ternary electrolytes) present. Excess of barium chloride, for example, gives rise to the formation of BaCl^+ , which reacts thus: $\text{SO}_4^{--} + 2\text{BaCl}^+ = \text{Ba}_2\text{Cl}_2\text{SO}_4$. The error in this case is in excess. Potassium sulphate gives KSO_4' , which with Ba^{++} gives $2\text{KSO}_4' + \text{Ba}^{++} = \text{BaK}_2(\text{SO}_4)_2$, giving an error in defect (Richards and Parker, A., 1895, ii, 370). The occlusion of barium chloride can be avoided to some extent by precipitation in dilute solutions and at as high a temperature as possible, conditions unfavourable to the formation of complex ions. The assertion of Allen and Johnston (A., 1910, ii, 650) that $\text{Ba}_2\text{Cl}_2\text{SO}_4$ can be freed from

chlorine by ignition could not be confirmed, as the presence of chloride was proved in all cases after fusion of the precipitate with carbonate. Similarly, the statement of Pregl ("Die quantitative organische Mikroanalyse," 1917, p. 29) that occluded barium chloride can be washed out after ignition of the precipitate, could not be confirmed. The authors recommend results to be corrected for the presence of chloride by fusion of the precipitate with sodium carbonate and estimation of the chlorine. The presence of nitrate gives rise to a greater error than chloride. Errors due to the occlusion of calcium, iron, and potassium are chiefly to be ascribed to the formation of complex ions. Phosphate is precipitated as barium phosphate along with the sulphate. The authors are of opinion that it is impossible to give general directions for the accurate estimation of sulphate in solutions. W. S. M.

Estimation of Sulphate as Strontium Sulphate. I. M. KOLTHOFF and E. H. VOGELZANG (*Pharm. Weekblad*, 1919, **56**, 159—161).—Following on their work on the precipitation of sulphates as barium sulphate (see preceding abstract), the authors have investigated the estimation of sulphate as strontium sulphate. Preliminary solubility determinations showed that strontium sulphate is practically insoluble in 50% ethyl alcohol. The sulphate is precipitated in the cold by 10% strontium chloride solution. An equal volume of 96% ethyl alcohol is added, and, after settling at the ordinary temperature, the precipitate is collected and washed with 50% alcohol. The moist filter is burned and ignited. Estimations were carried out in neutral solutions and in presence of hydrochloric acid, sodium acetate, ammonium chloride and nitrate, potassium chloride, sodium chloride and nitrate. Considerable errors in defect were observed. To eliminate the simultaneous precipitation of iron salts, sugar, glycerol, lactic and oxalic acids were added. These rendered filtration difficult without improving the results. The authors conclude that, in general, accurate results are not to be expected from this method. W. S. M.

Modifications of Pearce's Method for Arsenic. JOHN WADDELL (*J. Ind. Eng. Chem.*, 1919, **11**, 939—941).—The following alterations are made in Bennett's and Canby's modifications of Pearce's method (*A.*, 1899, ii, 519) in order to render them trustworthy. In Bennett's method, nitric acid should be added to neutralise any large excess of alkali in the solution, the latter then rendered slightly alkaline with sodium hydroxide, and acidified very slightly with acetic acid before the arsenic is precipitated as silver arsenate. Canby's method is modified in a similar way, except that in place of acetic acid, nitric acid is added in slight excess, and, after the addition of silver nitrate, this excess is neutralised by zinc oxide. W. P. S.

Reaction between Arsenious Oxide and Iodine. I. M. KOLTHOFF (*Pharm. Weekblad*, 1919, **56**, 621—634).—The reaction $\text{As}_2\text{O}_3 + 2\text{I}_2 + 2\text{H}_2\text{O} \rightleftharpoons \text{As}_2\text{O}_5 + 4\text{HI}$ is studied with reference to the

limits of hydrogen-ion concentration within which a definite end-point is obtained. The hydrogen-ion concentration is determined colorimetrically by means of various indicators. In the titration of $N/10$ - and $N/100$ -arsenious oxide solutions with iodine, the final acidity must lie between $10^{-11.0}$ and $10^{-5.0}$ mol. hydrogen ion per litre. In the titration of $N/10$ - and $N/100$ -iodine solutions with arsenious oxide solution, the initial limits are $10^{-9.0}$ and $10^{-5.5}$, and the final $10^{-8.0}$ and $10^{-6.0}$. The purity of the arsenious oxide used is best estimated by measurement of the conductivity of a saturated solution. The commonly occurring impurity is arsenic oxide, which may be estimated by means of the reaction of the solution with dimethyl-yellow and methyl-red. Neutral or weakly acid solutions of arsenious oxide are stable, and may be kept indefinitely without change of titre. In alkaline solutions, oxidation of arsenious to arsenic oxide takes place.

W. S. M.

Method for Estimation of Carbon by Wet Combustion, using Barium Hydroxide as Absorbent. P. L. HIBBARD (*J. Ind. Eng. Chem.*, 1919, **11**, 941—943).—A convenient method of procedure and apparatus for use in the method are described. The substance is oxidised by heating in a flask with chromic acid and sulphuric acid, and the resulting carbon dioxide is carried by a current of air into an excess of standard barium hydroxide solution; at the end of the operation, the excess of barium hydroxide is titrated with hydrochloric acid, using phenolphthalein as indicator. The air used is first passed through a soda-lime tube; after leaving the oxidation flask, the air carrying the carbon dioxide, etc., passes through a condensing tube, a tube filled with beads moistened with sulphuric acid, and a tube filled with amalgamated granulated zinc, before it enters the barium hydroxide solution; the latter is contained in an inclined flask, into which extends the lower end of a Meyer bulb tube.

W. P. S.

Microchemical Identification of Lead. G. DENIGÈS (*Bull. Soc. Pharm., Bordeaux*; from *J. Pharm. Chim.*, 1919, [vii], **20**, 159—160).—Soluble lead salts yield characteristic crystals of lead iodide when treated with a drop of potassium bromide solution and a drop of potassium iodide solution. With insoluble lead salts, the addition of a drop of sulphuric acid is necessary. Lead chromate, cyanide, and fluoride should be evaporated with hydrochloric acid, and metallic lead and lead sulphide with nitric acid, before the test is applied.

W. P. S.

Titrimetric Estimation of Lead. PAUL HOLMSEN (*Tidskr. Kemi Farm. Ter.*, 1919, **16**, 110—113).—A solution, not exceeding 100 c.c., containing 0.5—0.1 gram of lead, neutralised with ammonia, is acidified with 15 c.c. of acetic acid, 10 grams of ammonium acetate added, and the liquid warmed to 70—80°. The lead is precipitated by slowly adding 10 c.c. of ammonium molybdate solution, with constant stirring, warming for fifteen minutes, setting aside for thirty minutes, filtering, and washing with hot

water. The precipitate is treated with 50 c.c. of dilute sulphuric acid and hot water, 10 grams of pure zinc added, and boiled for ten minutes, filtered, washed with hot water, and the molybdenum in the filtrate titrated with 0.1*N*-permanganate. One c.c. of 0.1*N*-permanganate is equivalent to 0.007296 gram of lead.

CHEMICAL ABSTRACTS.

Microchemical Reactions with Thiosulphuric Acid. A. BOLLAND (*Compt. rend.*, 1919, **169**, 651—654).—Sodium thiosulphate gives crystalline precipitates, which are well defined when examined microscopically, with thallous nitrate, barium chloride, lead acetate, and benzidine. Sketches are given of the microcrystalline structure of these precipitates. In the case of barium chloride, the appearance of the precipitate varies with the experimental conditions. It is preferable, in this case, to use a concentrated solution of the thiosulphate.

W. G.

Electroanalysis of Copper without Platinum Electrodes. JUAN GUITERAS (*Anal. Fis. Quim.*, 1919, **17**, 209—216. See A., 1915, ii, 652, and 1916, ii, 199).—A copper cathode and a rotating anode of passive iron were employed. 0.1—0.2 Gram of electrolytic copper was dissolved in twenty drops of nitric acid for each estimation, and the various electrolytes were prepared by the addition of the following solutions: (1) 5 grams of disodium phosphate in water and 15 c.c. of concentrated ammonia solution; (2) 5 c.c. of 50% ammonium acetate solution and 15 c.c. of ammonia; (3) 3 grams of ammonium oxalate in water and 15 c.c. of ammonia; (4) 15 c.c. of formic acid solution (75 c.c. of water and 25 c.c. of formic acid, D 1.2) and 15 c.c. of ammonia; (5) 2 grams of citric acid in water and 15 c.c. of ammonia; (6) 2 grams of boric acid in water and 15 c.c. of ammonia. During electrolysis, the electrolyte was kept warm and the voltage gradually reduced from about 3 volts to 1.7—1.8 volts. The experiments were repeated with the constant voltage of one accumulator throughout. In all cases, the deposits on the cathode were coherent and the results satisfactory. Experiments in ammoniacal solutions of thiocyanate gave inaccurate results.

W. S. M.

New Separation of Aluminium and Vanadium. P. WENGER and H. VOGELSON (*Helv. Chim. Acta*, 1919, **2**, 550—553).—Methods are described for the quantitative separation of (1) aluminium and vanadium, (2) aluminium, iron, and vanadium. In the case of aluminium and vanadium the mixture of oxides is heated with six times its weight of anhydrous sodium carbonate, at first gradually, until the mass melts, and then at a higher temperature for three hours. The crucible and contents are allowed to cool somewhat, plunged into distilled water, and raised to the boiling point, when a clear solution of sodium aluminate and vanadate is obtained. The solution is made up to 500 c.c. with distilled water, raised to the boiling point, and treated with about ten times its weight of ammonium nitrate in small quantities. Aluminium hydroxide is pre-

precipitated, filtered, washed, ignited, and weighed as Al_2O_3 . The filtrate is acidified with hydrochloric acid, neutralised with ammonia, raised to the boiling point, and treated with barium chloride solution. Barium vanadate is precipitated; the precipitate is kept for twenty-four hours, filtered, washed with cold water, dried, ignited, and weighed as $\text{Ba}(\text{VO}_3)_2$. In the presence of iron a solution is made which is precipitated cold by ammonia. This precipitate, which contains iron and aluminium hydroxides and ammonium vanadate, is filtered, washed, ignited in a platinum crucible, mixed with six times its weight of sodium carbonate, and ignited as before. The fused mass is dissolved in water to which 1 gram of sodium carbonate has been added. The iron left insoluble as oxide is filtered off and weighed, and the filtrate treated as described above. The results of the analyses are extremely good. J. F. S.

Sulphite Method for the Separation and Estimation of Gallium when Associated with Zinc. LYMAN E. PORTER and PHILIP E. BROWNING (*J. Amer. Chem. Soc.*, 1919, **41**, 1491—1494).—Gallium is conveniently precipitated from neutral or acid solutions of zinc by adding 4 or 5 c.c. of ammonium hydrogen sulphite solution (made from 1:4 ammonia) to 200 c.c. of the zinc solution and boiling. If gallium is present it will be precipitated in granular form and can be filtered and washed by decantation. The precipitate is dissolved in a few drops of hydrochloric acid, diluted to 200 c.c. with water, and reprecipitated as before. This is filtered, washed, ignited, and weighed as Ga_2O_3 . The potassium ferrocyanide test is sensitive to 0.0002 gram of gallium, and may be used to detect this element in the presence of zinc. If sodium or ammonium hydrogen sulphite is added to such a cold solution and then potassium ferrocyanide, there will be no precipitation, but on the addition of a few drops of hydrochloric acid the gallium will be precipitated, but not the zinc. J. F. S.

Hydrochloric Acid Colour Method for Estimating Iron. J. C. HOSTETTER (*J. Amer. Chem. Soc.*, 1919, **41**, 1531—1543).—A method has been elaborated by which the yellow colour produced by dissolving ferric chloride in hydrochloric acid may be used for the estimation of iron. This involves the comparison of the tint with standard tints. The temperature-coefficient for the colour varies 2—3% per degree, depending on the concentration of the iron and probably also on the acidity. The colour developed by a given amount of iron varies with the acid concentration, reaching the maximum intensity at 26—28% of hydrochloric acid. The relative increase produced by acid is greater the higher the concentration of iron; this is especially true above 20% of hydrochloric acid, but below this concentration the relative change is independent of the iron content. Inasmuch as solutions must frequently be boiled in order to ensure complete solution of the iron present as "scale," the use of constant boiling acid is recommended, and its use has been found to be altogether satisfactory. The effect of salts on the colour indicates that sulphates cause bleaching, and chlorides intensification; a detailed study of the effect of calcium chloride

shows that an intensification of 2.5 may be attained by the addition of this salt; consequently, when testing for iron in a very soluble chloride the standard iron solution must be made up to the same salt concentration. J. F. S.

A Method for the Quick Estimation of the Nickel-Iron in Meteorites. G. T. PRIOR (*Min. Mag.*, 1919, 18, 349—353).—The classification of meteorites based on the amount of nickel-iron they contain and the ratio of iron to nickel in this metallic portion (A., 1916, ii, 635) requires a rapid method applicable to meteoric stones for the estimation of these quantities. The sieved material is separated into attracted and unattracted portions by a magnetic comb. The former is digested with dilute aqua regia, and the insoluble silicate which was entangled with the metal separated off; estimations of the silica and sulphur give the amounts of the soluble silicate (olivine) and the troilite (FeS); these, deducted from the weight of the attracted portion, give the weight of the nickel-iron. Nickel is estimated by precipitation with dimethylglyoxime in an aliquot portion of the solution. The method is applied to the partial analysis of seventeen meteoric stones, and the results (percentage of nickel-iron, and ratio of Fe+Co:Ni) are tabulated. L. J. S.

Electroanalysis of Nickel without Platinum Electrodes. EMILIO FERNÁNDEZ-ESPINA (*Anal. Fis. Quim.*, 1919, 17, 199—205. See A., 1916, ii, 494).—A copper cathode and a rotating iron anode, rendered passive by immersion in nitric acid, were employed. About 0.1 gram of pure nickel was dissolved in 15 drops of nitric acid and the solution evaporated to dryness after the addition of 18 drops of sulphuric acid. The various electrolytes were prepared by the further addition of the following to the nickel sulphate thus obtained: (1) sodium phosphate solution and 10 c.c. of concentrated ammonia solution; (2) 5 c.c. of 50% ammonium acetate solution and 10 c.c. of ammonia; (3) 15 c.c. of 25% formic acid and 15 c.c. of ammonia; (4) 5 grams of ammonium oxalate in 15 c.c. of water and 15 c.c. of ammonia; (5) 2 grams of crystallised boric acid and 15 c.c. of ammonia; (6) 2 grams of tartaric acid and 10 c.c. of ammonia. In each case a convenient quantity of water was also added. During the electrolysis the electrolyte was kept slightly warm, and the current increased progressively from 0.4 ampere to about 0.8 ampere. The results were moderately satisfactory in all cases except the last, in which the iron of the anode appeared to be dissolved and deposited with the nickel. W. S. M.

Estimation of Tin. F. LE NAOUR (*Ann. Chim. anal.*, 1919, [ii], 1, 308—309).—The author finds that ignited stannic oxide (SnO_2) is not appreciably hygroscopic, although Bertiaux has stated the contrary (A., 1918, ii, 408). One gram of the oxide absorbed only 2 mg. of moisture when exposed to the atmosphere for eighteen hours. W. P. S.

The System *n*-Butyl Alcohol-Acetone-Water. JOSEPH REILLY and EDGAR W. RALPH (*Sci. Proc. Roy. Dublin Soc.*, 1919, 15, 597—608).—The densities of a series of *n*-butyl alcohol-acetone-

water mixtures have been determined, and graphs from these prepared with rectangular and triangular co-ordinates. From these results the composition of an unknown mixture may readily be obtained with a fair degree of accuracy if a density determination and the estimation of one constituent are made. The limit of solubility of *n*-butyl alcohol in water at 20° is 7.9% and of water in *n*-butyl alcohol 20%. The maximum contraction for mixtures of *n*-butyl alcohol and water within the range of solubility at 20° is 0.74%.

Acetone and *n*-butyl alcohol are miscible in all proportions, there being a slight increase of volume on mixing. W. G.

Estimation of Methyl Chloride in Gas Mixtures. V. C. ALLISON and M. H. MEIGHAN (*J. Ind. Eng. Chem.*, 1919, **11**, 943—946).—The method proposed depends on the solubility of methyl chloride in glacial acetic acid, and is particularly useful for estimating the proportion of methyl chloride in chlorinated natural gas. A measured volume of the gas is led six times into a Hempel pipette containing glacial acetic acid, and then returned to the measuring burette; the contraction in volume gives the quantity of methyl chloride present. One volume of acetic acid absorbs more than 40 volumes of methyl chloride and 4 volumes of natural gas, but the solubility of the latter is very small when the gaseous mixture contains 40% or more of methyl chloride. The results obtained agree with those found by the partial pressure method (A., 1915, ii, 100). W. P. S.

Sulphonal. A. FALCK (*Pharm. Zentr.-h.*, 1919, **60**, 409—416).—The solubility of sulphonal in various solvents was found to be as follows, the figures representing grams of solvent required to dissolve 1 gram of the substance: Water at 15°, 423; water at 100°, 8; 90% alcohol at 15°, 60; ether at 17°, 79; chloroform at 20°, 3.3; methylene chloride, 2.8; benzene at 17°, 12.7; ethyl acetate, 13.7; toluene, 19.3; carbon tetrachloride, 110; carbon disulphide, 440; 2% sodium chloride solution at 18°, 440. Owing to the fact that sulphonal begins to volatilise at 60° and is very appreciably volatile in the presence of water-vapour, solutions containing the substance should not be concentrated by evaporation before the quantity of sulphonal is estimated. The sulphonal should be extracted with chloroform and the extract evaporated at a low temperature. Sulphonal is stable for a long time in the presence of decomposing organic matter, and characteristic crystals may be obtained from its ether or chloroform solution. W. P. S.

The Estimation of the Volatile Fatty Acids by an Improved Distillation Method. JOSEPH REILLY and WILFRED J. HICKINBOTTOM (*Sci. Proc. Roy. Dublin Soc.*, 1919, **15**, 513—538).—It is known that when dilute solutions of organic fatty acids are distilled certain regularities are observed. Various forms of distillation constants have been suggested by Duclaux (A., 1896, ii, 504), Naumann and Müller (A., 1901, i, 204), and Stein (A., 1913, ii, 670)

to express such regularities. These constants may be derived from Nernst's law of distribution, and on this law the authors base a discussion of the theory of distillation of dilute solutions. A method of distillation at constant volume, in which only small changes in concentration occur, is recommended, and an apparatus is described in which this process may be simply and satisfactorily carried on. The distillation constants of the fatty acids from formic to octoic have been determined, and it is shown that there is a definite relationship between the rate of distillation and the molecular constitution of these acids. Acids containing a branched carbon chain have higher constants than normal acids of the same molecular weight.

The methods of calculation are quite satisfactory for establishing the identity and purity of a solution of a single volatile fatty acid, and also give fairly accurate results in the analysis of "two-acid" mixtures. The results with mixtures of three acids are not so satisfactory. The method may be applied to fermentation products. By suitable modification of the apparatus the distillation constants for the volatile acids in butter and coco-butter can be determined and utilised for detecting the presence of adulterants.

W. G.

Estimation of Lactic Acid by Oxidation. O. SCHUPPLI (*Mitt. Lebensmittelunters. u. Hyg.*, 10, 44—47; from *Chem. Zentr.*, 1919, ii, 894).—Szeberényi's process (A., 1918, ii, 138) gives trustworthy results in aqueous solution, but is not applicable to wines.

H. W.

Naphtharesorcinolcarboxylic [1:3-Dihydroxynaphthalene-2-carboxylic] Acid as a Reagent for Glycuronic Acid. Y. ASAHINA and C. HASEGAWA (*Yakugakuzasshi [J. Pharm. Soc. Japan]*, 1919, No. 448, 484—489).—1:3-Dihydroxynaphthalene-2-carboxylic acid, which cannot be preserved unchanged for any length of time, is best kept in the form of the barium salt, from which it is prepared, when required, by treatment with hydrochloric acid. The authors also describe the preparation of this reagent from phenylacetic acid by Metzner's method (A., 1898, i, 152).

CHEMICAL ABSTRACTS.

Detection of Small Amounts of Chloral in the Presence of Chloroform and Formalin Embalming Fluid. A. O. GETTLER (*Proc. Soc. Exp. Biol. Med.*, 1919, 16, 110—116; from *Physiol. Abstr.*, 1919, 4, 255).—When kept at the ordinary temperature for half an hour with sodium carbonate and phloroglucinol, chloral develops lilac to orange, to blood orange, to deep red colorations, the shade depending on the amount of chloral present. Chloroform does not give this reaction; formaldehyde and acetaldehyde give a red colour. With resorcinol and sodium carbonate, chloral gives a red colour and a green fluorescence, the latter even in dilute solution; chloroform does not yield the green fluorescence, whilst substances of an aldehydic character do not give the reaction.

H. W.

Estimation of Acetone, Methyl Alcohol, and Furfuraldehyde in the Presence of Each Other. H. PRINGSHEIM and E. KUHN (*Zeitsch. angew. Chem.*, 1919, **32**, 286—290).—The furfuraldehyde is precipitated by treating a portion of the mixture with phenylhydrazine in the presence of sodium acetate, the precipitate being collected, dried under reduced pressure over sulphuric acid, and weighed; its weight multiplied by 0.516 gives the corresponding quantity of furfuraldehyde. The filtrate from the phenylhydrazone precipitate is distilled with the addition of an excess of hydrochloric acid, and the distillate redistilled from magnesium oxide. In this second distillate, the methyl alcohol is estimated by oxidation with dichromate and sulphuric acid in the cold. Provided that the oxidation mixture contains about 2% of potassium dichromate (for example, 25 c.c. of distillate containing not more than 0.2 gram of methyl alcohol, 50 c.c. of *N*/1-potassium dichromate solution, and 50 c.c. of dilute sulphuric acid), the methyl alcohol is oxidised completely in eighteen hours, but the acetone is not attacked. The acetone is estimated iodometrically in a separate portion of the distillate. [See, further, *J. Soc. Chem. Ind.*, 1919, 877A.] W. P. S.

Some Iodometric Estimations. Preliminary Studies on a Micro-method for the Estimation of Acetone. MALTE LJUNGDAHL (*Biochem. Zeitsch.*, 1919, **96**, 325—345. Compare A., 1917, ii, 584).—The author points out and discusses in detail the conditions which must be observed in the iodometric titrations employed in his micro-method for the estimation of acetone in order to ensure accuracy. S. S. Z.

A Micro-method for the Estimation of the Total Acetone in Blood. MALTE LJUNGDAHL (*Biochem. Zeitsch.*, 1919, **96**, 345—362).—The principle of the method consists in distilling the acetone from the blood collected in a capillary tube into a solution containing an excess of iodine and alkali. The solution is then boiled in order to convert the acetone into chloroform, and the residual iodine is estimated by titrating with thiosulphate. S. S. Z.

Detection and Estimation of Traces of Hydrocyanic Acid in Complex Mixtures. L. CHELLE (*Bull. Soc. Pharm., Bordeaux*, 1919, 140; from *J. Pharm. Chim.*, 1919, [vii], **20**, 156—157*).—The solution containing hydrocyanic acid or a cyanide is acidified with sulphuric acid, and air, free from carbon dioxide, is aspirated through the solution; the air is then passed through a vessel containing alkali hydroxide, which absorbs the hydrocyanic acid, and the latter is estimated subsequently by the ferrocyanide or ammoniacal silver iodide method. The whole of the hydrocyanic acid is removed from 50 c.c. of solution containing 0.48 to 54 mg. of hydrocyanic acid when the air current is maintained for three hours at the rate of 75 litres per hour. W. P. S.

* See also *Compt. rend.*, 1919, **169**, 973—975.

Detection and Estimation of Traces of Thiocyanate in Complex Mixtures. L. CHELLE (*Bull. Soc. Pharm., Bordeaux*, 1919, 150; from *J. Pharm. Chim.*, 1919, [vii], 20, 158—159*).—The thiocyanate is oxidised to cyanide by means of potassium chromate in sulphuric acid solution; the hydrocyanic acid is then separated by passing a current of air through the solution, as described in the preceding abstract. W. P. S.

The Transformation of Hydrocyanic Acid into Thiocyanic Acid in the Course of Cadaverous Putrefactions. Experiments made in vitro. L. CHELLE (*Compt. rend.*, 1919, 169, 726—728).—From experiments with blood in vitro, the author shows that, during putrefaction, hydrocyanic acid or its salts are converted into thiocyanic acid, and that this change is very rapid. Hydrocyanic acid may be regenerated from the thiocyanic acid by oxidation with chromic acid. W. G.

Test to Distinguish between Caffeine and Theobromine. FREEMAN P. STROUP (*Amer. J. Pharm.*, 1919, 91, 598—599).—A small portion of the alkaloid is spread in a thin film on a white porcelain surface, and two drops of a solution of 1 gram of potassium dichromate in 20 c.c. of concentrated sulphuric acid are placed in the centre of the film. With caffeine, the colour of the reagent almost immediately changes to bright bluish-green, whilst with theobromine the yellow colour of the reagent changes first to dark purple, then gradually to purple-green, and later to the same bluish-green tint given by caffeine. If desired, the test may be carried out in the reverse way, the alkaloid being added to two drops of the reagent, but in both cases the time required for the production of the green colour is very much less with caffeine than with theobromine. W. P. S.

Examination of Commercial Samples of Nicotine. PERCIVAL J. FRYER and C. HENRY FRYER (*Analyst*, 1919, 44, 363—369).—Commercial nicotine is sometimes adulterated with pyridine, and the presence of this substance makes it impossible to estimate the nicotine by titration or by precipitation with silicotungstic acid. The difference in the refractive indices of nicotine and pyridine, however, provides a method for the estimation. The following figures are taken from tables in the original, which show the refractive index of aqueous solutions containing 1 to 100% of either substance in differences of 1%.

If a sample contains pyridine, the percentage of nicotine calculated from the titration will be larger than the percentage calculated from the refractive index, and the difference between the percentages will give approximately the percentage of pyridine present. Another method is as follows: 25 grams of the sample are diluted with water to 100 c.c. and heated at 99° for ten minutes, cooled, and, after some hours, the refractive index of the surface liquid is determined. Under these conditions, the greater part of

* See also *Compt. rend.*, 1919, 169, 973—975.

Nicotine. Per cent.	n_D^{15} .	Pyridine. Per cent.	n_D^{15} .
100	1.5300	100	1.5136
95	1.5255	95	1.5088
90	1.5193	90	1.5028
85	1.5118	85	1.4960
80	1.5035	80	1.4884
75	1.4950	75	1.4799
70	1.4852	70	1.4710
65	1.4743	65	1.4616
60	1.4663	60	1.4516
55	1.4523	55	1.4414
50	1.4413	50	1.4317
45	1.4303	45	1.4219
40	1.4193	40	1.4123
35	1.4083	35	1.4025
30	1.3976	30	1.3927
25	1.3868	25	1.3829
20	1.3760	20	1.3731
15	1.3652	15	1.3632
10	1.3546	10	1.3532
5	1.3443	5	1.3435
0	1.3341	0	1.3341

the nicotine separates as a heavy oil, whilst the pyridine remains in solution. In the case of pure nicotine, the refractive index obtained shows, according to the above table, 9.7% of nicotine; when pyridine is present to the extent of more than 10%, this figure is increased, and reference to the following table will give the approximate extent of the adulteration:

Pyridine. Per cent.	n_D^{15} of aqueous liquid.
0	1.3540
10	1.3558
15	1.3587
20	1.3616
25	1.3640
30	1.3662
35	1.3684
40	1.3705

The quantity of pyridine present may also be estimated by a fractional distillation method; 100 c.c. of the sample (adjusted to 95% of nicotine, as shown by the refractive index, by the addition of water or by concentration over sulphuric acid) are distilled from a standard Engler flask up to 150°. The volume of the distillate is noted (it does not exceed 5 c.c. in the case of pure nicotine), the refractive index is determined, and the percentage of pyridine found from the following table:

n_D^{15} of distillate.	Pyridine. Per cent.
1.357	0
1.366	1
1.401	5
1.436	10
1.454	15
1.467	20
1.477	25

Identification and Estimation of Solanine. DEJUSSIEU (*Bull. pharm. sud-est.*, 1919, **24**, 357—361).—The method of Bellot (*Arch. Med. Pharm. milit.*, April, 1914) for the estimation of solanine in potatoes is criticised, because it involves the use of boiling water acidified with sulphuric acid in extracting the alkaloid. The author directs attention to the fact that solanine is an unstable base which is readily hydrolysed by hot dilute acids, yielding dextrose, rhamnose, galactose, and solanidine. A number of authorities are cited in support of this criticism. With reference to the identification of the alkaloid, the work of Ogier ("Traité de Toxicologie") is quoted, who states that hot dilute solutions of solanine in ethyl or amyl alcohol gelatinise on cooling, and that this property is particularly characteristic of this base.

CHEMICAL ABSTRACTS.

The Colorimetric Estimation of Hæmoglobin. BARNETT COHEN and ARTHUR H. SMITH (*J. Biol. Chem.*, 1919, **39**, 489—496).—The general technique recommended by Palmer (A., 1918, ii, 88) is employed, but the standard solution is acid hæmatin, as in the Sahli method ("Lehrbuch Klin. Untersuch. Methoden," 1909, 845). The hæmoglobin of whole blood is converted into acid hæmatin with hydrochloric acid and compared with a standard in a colorimeter of the Autenreith-Hellige pattern. An acid hæmatin standard, prepared from the blood of one species, may be used in the colorimetric estimation of hæmoglobin in the blood of a variety of other species.

J. C. D.

Technique of Chemical Blood Analysis. II. A Comparison between Macro- and Micro-methods. M. RICHTER-QUITTNER (*Biochem. Zeitsch.*, 1919, **96**, 92—106).—A critical comparison against macro-methods of some well-known micro-methods employed in blood analysis. The conclusion arrived at is that, with some modifications, these methods are capable of giving accurate results.

S. S. Z.

Analysis of Gastric Juice. CERBELAUD (*Union pharm.*, 1918; from *Ann. Chim. anal.*, 1919, [ii], **1**, 299—301).—The acidity is estimated by titration with *N*/10-sodium hydroxide solution, using phenolphthalein as indicator. The total chlorine is estimated by treating 5 c.c. of the gastric juice with 2 c.c. of sodium hydroxide solution (D 1.332) and 2 c.c. of 5% potassium permanganate solution; 10 c.c. of concentrated nitric acid are then added, the mixture, after fifteen minutes, is diluted with 50 c.c. of water, and the chlorine titrated with silver nitrate and thiocyanate solutions. Organic chlorine and fixed chlorine are estimated together in the same way after the gastric juice has been evaporated to dryness, and the residue heated at 100° for one hour. Fixed (mineral) chlorine is titrated in the ash obtained by evaporating the gastric juice and incinerating the dry residue at a low temperature; in this case, the treatment with alkaline permanganate and nitric acid is also employed.

W. P. S.

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ERRATA.

VOL. XCII (ABSTR., 1907).

Page	Line	
i. 216	bottom	<i>for "m.p. 240°" read "m.p. 204°."</i>

VOL. CIV (ABSTR., 1913).

Page	Col.	Line	
i. 780		17	} <i>for "Nitrous oxide" read "Nitric oxide."</i>
		19	
		20	
		10*	
		9*	
		4*	
ii. 1210	i.	32	} <i>for "Nitrous oxide" read "Nitric oxide."</i>
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ii. 1337		28	
ii. 1390	ii.	19*	

VOL. CVIII (ABSTR., 1915).

Page	Col.	Line	
i. 326		18	} <i>for "Nitrous oxide" read "Nitric oxide."</i>
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ii. 934	ii.	16	
ii. 1079		8-10	<i>the entry "behaviour of various substances with (PANZER), A., i, 326," should be transposed to line 19 (under nitrogen dioxide).</i>

VOL. CXVI. (ABSTR., 1919).

Page	Line	
i. 357	15	<i>for "antipyrine" read "1-phenyl-3-methyl-5-pyrazolone."</i>
i. 402	1	<i>"BRENER" read "BREUER."</i>
i. 559	13	<i>"ERIC DODDRELL EVANS" read "ERIC DODDRELL EVENS."</i>
ii. 261	13	<i>"ten" read "two."</i>
ii. 263	24	<i>"ALBERT NOYES" read "WILLIAM A. NOYES, jun."</i>
ii. 312	20	<i>"KIRCHOF" read "KIRCHHOF."</i>
ii. 327	7*	<i>"LANGHAUS" read "LANGHANS."</i>
ii. 351	15	<i>"ZEPFEL" read "ZIPFEL."</i>
ii. 443	3*	<i>"HORSH" read "HORSCH."</i>
ii. 446	7*	<i>after "421.73°" insert "on the platinum resistance scale."</i>
ii. 529	15*	<i>for "chloroform" read "iodoform."</i>

* From bottom.